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AEC RESEARCH AND DEVELOPMENT REPORT

PROCESS DEVELOPMENTS IN THE MANUFACTURE OF URANIUM HEXAFLUORIDE

JULY 1957 - JUNE 1959

UNION CARBIDE NUCLEAR COMPANY
A DIVISION OF UNION CARBIDE CORPORATION
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PROCESS DEVELOPMENTS IN THE MANUFACTURE OF URANIUM HEXAFLUORIDE

July 1957 · June 1959

UNION CARBIDE NUCLEAR COMPANY
Division of Union Carbide Corporation
OAK RIDGE GASEOUS DIFFUSION PLANT
Oak Ridge, Tennessee

PROCESS DEVELOPMENTS IN THE MANUFACTURE OF URANIUM HEXAFLUORIDE

July 1957 – June 1959

ABSTRACT

Studies made of methods for the manufacture of uranium hexafluoride at the Oak Ridge Gaseous Diffusion Plant between July 1, 1957, and June 30, 1959, are reported. Among the methods and equipment described are the following: The direct fluorination of uranium ore concentrates, purification of uranium hexafluoride by sorption and distillation, a Karbate distillation column for aqueous hydrogen fluoride, and methods for the recovery of uranium and hydrogen fluoride from magnesium fluoride slag generated in the preparation of uranium metal. The results of experiments with laboratory, pilot plant, and plant-scale equipment are presented.

This report is a compilation of material from the Oak Ridge Gaseous Diffusion Plant Quarterly Reports for the period concerned. It is a continuation of Reports K-1347, Parts 1 and 2, which describe feed manufacture development work between January 1, 1947, and June 30, 1957.

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PROCESS DEVELOPMENTS IN THE MANUFACTURE OF URANIUM HEXAFLUORIDE

July 1957 – June 1959

PREFACE

This report is a compilation of information which appeared originally in the Oak Ridge Gaseous Diffusion Plant Quarterly Reports between July 1, 1957, and June 30, 1959. The material presented has been edited only enough to provide continuity and clarity. Table and figure numbers have not been changed from the original text; therefore, care should be exercised in referring from the text to tables and figures. It should be remembered that all of the information presented is in the form of a series of preliminary progress reports. In many instances, the data had not been fully evaluated at the time the report was written and were subject to revision or correction; therefore, there may be discrepancies between statements made in succeeding quarters.

This report is a continuation of Reports K-1347, Parts 1 and 2, which were a compilation of progress reports between January 1, 1949, and June 30, 1957.

A bibliography is given at the end of this report which lists reports on manufacture of uranium hexafluoride published during the period covered by the report. No attempt has been made to associate the reports in the bibliography with the material in the text.

JULY 1, 1957, THROUGH SEPTEMBER 30, 1957

FLUIDIZATION

Fluid-Bed Hydrofluorination

Operation of the two-stage stirred fluid-bed hydrofluorination unit described previously was continued. Frequent plugging of the powder crossover between the two stages and high dust carryover in the off-gases from the first stage, which permitted short circuiting of about 25% of the stage 1 powder directly to the product receiver, made it necessary to alter the pilot-plant equipment as shown in figure F-6. A hopper and feed screw assembly was installed between the reactors to separate the gas streams and to permit the removal of the gases and solids from the first stage through a common line. In addition, parallel filters were installed in each of the outlet gas lines so that operation of the unit would not have to be suspended during filter blowbacks. These equipment modifications eliminated the difficulties, and the unit has been operated successfully with ground Hanford continuous-calciner oxide, pot-calcined Port Hope oxide, and Anaconda acid-leached, ammonia-precipitated ore concentrate.

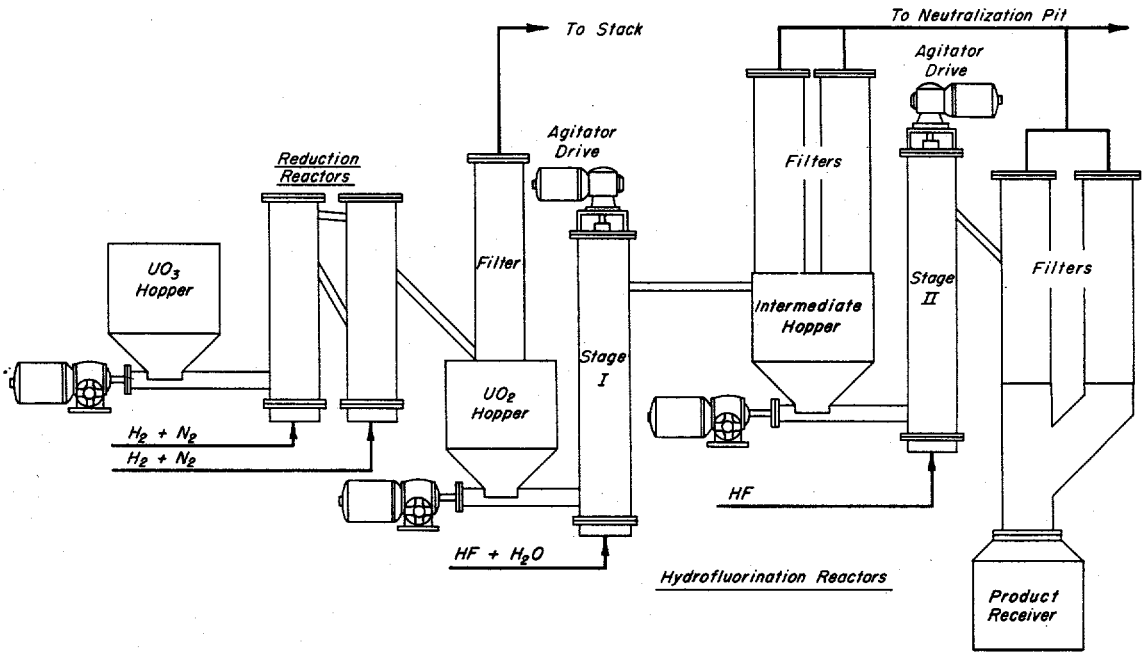

FIGURE F-6
Agitated Fluid Bed Pilot Plant

Hanford Continuous-Calciner Oxide. The initial studies in the revised unit were made with Hanford continuous-calciner oxide which contained 1,600 ppm. of sulfur. A solids feed rate of about 42 pounds per hour per cubic foot of bed* was employed for most of the tests, and the hydrogen fluoride fed to the first reactor stage was diluted with water to simulate the conditions expected with series gas flow. The overall hydrogen fluoride excess, based on the outlet gas concentration, ranged from 6 to 17%.

It can be seen from the data, table F-14, that the highest conversion to uranium tetrafluoride in the

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* The volume of each reactor stage is about 1/2 cubic foot.

first stage was obtained with a reactor wall temperature of 550 or 650°F. At 750°F., a significant conversion drop was noted; this was probably due to the back reaction of the uranium tetrafluoride with water at the higher temperature. In the second stage, however, the concentration of water in the fluidizing gas was lower, and the highest temperature tested, 940°F., gave the best overall conversion, 93.6%. When the concentration of hydrogen fluoride in the inlet gas to the second stage was decreased from 100 to 73%, the conversion dropped to 89.4%.

TABLE F-14
Fluid-Bed Hydrofluorination of Pulverized Continuous-Calciner Oxide (1,600 ppm. of Sulfur)

			Stage 1					Stage 2				
Run No.	Reduction Temp., °F.	UO_2 Feed Rate, lb./cu.ft./hr.	Temp., °F.	HF Inlet Conc., %	HF Outlet Conc., %	HF Excess, %*	Conversion To UF_4, %	Temp., °F.	HF Inlet Conc., %	HF Outlet Conc., %	Conversion To UF_4, %	UO_2F_2, %
1	1050	52.2	550	56	23.6	14.0	63.5	650	100	92	84.2	2.6
2	1050	41.7	650	42	18.7	10.5	59.6	850	100	89	91.3	0.1
3	1050	33.6	750	56	17.6	10.0	51.9	850	100	87	89.8	1.3
4	1050	41.9	650	60	22.7	16.0	66.7	850	100	90	91.5	1.0
5	1050	40.5	550	61	23.7	17.0	70.2	750	100	87	91.5	0.1
6	1050	41.3	550	56	14.4	8.0	66.5	940	100	89	93.6	0.4
7	1050	46.4	550	60	11.9	6.0	65.3	950	73	58	89.4	1.0

* Equivalent excess for a plant reactor line.

Port Hope Oxide. Limited studies with Port Hope oxide which contained 220 ppm. of sulfur showed this material to be extremely reactive in the hydrofluorination step. Employing a feed rate of 56.8 pounds of uranium dioxide per hour per cubic foot of bed, a hydrogen fluoride excess of 4%, and temperatures of 570 and 850°F. in stages 1 and 2, respectively, an overall conversion to uranium tetrafluoride of 98% was obtained. The product from the first reactor stage contained about 47% uranium tetrafluoride.

Future Studies. Future work will be directed toward the optimization of the mechanical features of the unit, such as the agitator design, the agitator speed, and the support plate design, in addition to the evaluation of special batches of uranium trioxide and various ore concentrates.

Ore Concentrate Processing

Preparation of Uranium Hexafluoride. Approximately 1,500 pounds of uranium hexafluoride has been prepared from Anaconda acid-leached, ammonia-precipitated ore concentrate by reduction and hydrofluorination in the fluid-bed pilot plant, figure F-6, followed by fluorination in the 4-inch diameter tower reactor. The concentrate was extremely low in density, bulk and packed densities of 0.5 and 0.7 g./cc., respectively, and contained 69.6% uranium, 40 ppm. molybdenum, and 174 ppm. vanadium. Other impurities included 0.65% iron, 0.1% calcium, 0.24% magnesium, and less than 0.01% sodium.

The ore exhibited a high reactivity in both the reduction and the hydrofluorination steps. Although the feed rate to the reduction reactor was low, approximately 40 pounds of concentrate per cubic foot of bed per hour, temperature measurements showed that essentially no reaction took place in the second stage, thus indicating that the feed rate could be at least doubled. The only operating problem exhibited in the reduction step, other than the low storage capacity of the hopper and some difficulty in maintaining a powder seal, was the poor fluidization properties of the powder as evidenced by a wide spread in powder temperatures in the reactor. Changing the superficial gas velocities over a range of 0.4 to 0.9 foot per second did not improve the fluidization.

Essentially complete conversion of the reduced concentrate to uranium tetrafluoride was obtained in a single reactor stage with a feed rate of 104 pounds of oxide per hour per cubic foot of bed and a reactor wall temperature of 550°F. This hydrofluorination rate is approximately twice that obtained with the best oxide studied to date. Near the end of the tests, the agitator in the first hydrofluorination reactor jammed on three separate occasions. No reasons for the first two failures were found, in that neither bed caking nor obvious mechanical difficulties were observed; however, inspection of the reactor after the third failure showed that the powder had caked and formed small, dense lumps. The caking may have been caused by the use of a spiral type agitator, with a minimum of cross supports, in place of the reinforced spine type used previously.

The fluorination of the uranium tetrafluoride to uranium hexafluoride was accomplished in the 4-inch diameter pilot-plant fluorination tower. An overall conversion to uranium hexafluoride of 92% was attained with an average feed rate of 39 pounds of uranium tetrafluoride per hour, the maximum obtainable with the screw feeder. With the exception of two cases of plugging at the top of the tower after 23 and 36 hours of operation, respectively, the unit operated well. The formation of the caked material in the reactor and the high ash rate were probably due to the relatively low tower wall temperatures of 650°F. and less, which resulted from the low powder feed rate.

Samples of the uranium dioxide, uranium tetrafluoride, and uranium hexafluoride prepared in the tests have been submitted to the laboratory for determination of the impurity content.

Purification. It is planned to start distillation studies with the uranium hexafluoride prepared from the Anaconda acid-leached, ammonia-precipitated ore concentrate as soon as the installation of a packed column is complete. In addition, a series of bench-scale tests is being made to determine whether the molybdenum and vanadium present in the acid-leached, ammonia-precipitated ore concentrate can be removed by the formation of volatile compounds of these elements prior to the fluorination of the concentrate to uranium hexafluoride. Preliminary results indicate that the vanadium content of the concentrate can be reduced from 250 to about 10 ppm. by hydrofluorination of the unreduced concentrate at 1100°F. followed by reduction with hydrogen and a final hydrofluorination at the same temperature. The molybdenum content can be reduced from an initial concentration of 40 ppm. to 1 to 5 ppm. by the same treatment or by the standard reduction-hydrofluorination sequence employing a final hydrofluorination temperature of about 1100°F. With a hydrofluorination temperature of only 770°F., however, essentially no decontamination was noted. The laboratory analyses needed to determine the efficiency of the latter treatment with respect to vanadium removal are contradictory and must be checked.

Fluid-Bed Fluorination. The feasibility of employing a fluid-bed reactor for the fluorination of uranium tetrafluoride prepared from sodium precipitated ore concentrate is being investigated. Fused fluorination tower slag obtained in earlier tests with Anaconda carbonate leached ore was pulverized, mixed with minus 200 mesh magnesium fluoride slag, and fluorinated in a 6-inch diameter, single-stage, stirred fluid-bed unit. The starting mixture contained 23.9% uranium and 7.0% sodium.

The initial test was made with a solids feed rate of 15.4 pounds per hour, a wall temperature of 920°F., a fluorine concentration of 85%, and a superficial gas velocity of 0.1 foot per second. No operating difficulties were encountered during the run, and the solids discharged from the reactor contained only 1.8% uranium. The sodium content of this ash was 9.0%, while that of the material remaining in the reactor was 6.5%, thus indicating that the sodium fluoride particles might be separated from the magnesium fluoride carrier to some extent by air classification.

Further studies are planned as soon as additional sodium-precipitated ore concentrated is received.

Miscellaneous Studies

Fluorination Tower. Use of the 4-inch diameter pilot-plant fluorination tower on a production basis to recover uranium as uranium hexafluoride from slightly enriched uranium oxides (up to 1.6% U-235) was continued. During the period, a total of 17,074 pounds of uranium hexafluoride was prepared in 452 operating hours. The average conversion of the oxide to uranium hexafluoride was 94.1%.

Hydrogen Fluoride Still. The Karbate reboiler-condenser test unit was dismantled for inspection after 3,700 hours of operation with boiling hydrogen fluoride-water azeotrope. The heat transfer surfaces of the reboiler and bayonet were clean, and no visible attack was noted; however, a weight gain of 0.5% was noted for both the condenser and reboiler bayonets over the last 1,126 hours of operation. The still was reassembled, and after 400 hours of operation, the flange on the reboiler flange was tightened in order to stop a small gasket leak. Soon after tightening the flange, a small leak was detected in the flange material. This leak differed from the seepage leaks noted previously, in that the exterior surface of the flange contained a barely noticeable crack which was about 1/2-inch long and ran vertically between the flange faces. The carbon contents of two samples of scale, which formed over the leak, were 28.7 and 38.9%, thus indicating that either the carbon or the phenol formaldehyde filler was being removed from the Karbate by the acid and remained as a solid deposit when the acid vaporized from the flange. It is possible that the leak was caused by the compression, but the fact that the hairline crack did not extend to either flange face, and that a high concentration of carbon was found in the scale, infer that the crack may have been caused by acid deterioration of the Karbate. The leak was small in that only 2.5 pounds of inventory was lost over a 10-day period.

A smaller reboiler-condenser unit fabricated of Impervite was examined after 1,817 hours of operation. The heat transfer surfaces in the reboiler and the condenser were clean, and no visible attack was noted. The tests on both stills are being continued.

Recovery of Uranium from Magnesium Fluoride Slag. The investigation of the recovery of uranium from magnesium fluoride bomb slag by direct fluorination was completed with a series of runs in the vibrating-tray pilot plant. Employing pulverized slag from the Paducah metals plant, five runs were made with residence times ranging from 0.8 to 1.7 hours, feed rates of 18.5 to 42 pounds per hour, and a tray temperature of 1000°F. A gas feed of about 85 mol percent fluorine was used in all but the final run in which the feed gas was diluted with air to 45 mol percent fluorine. The uranium content of the slag was reduced from about 5% to 0.19 to 0.35 weight percent with the more finely ground powders containing the least uranium, table F-15. All analytical results were obtained by complete dissolution of the samples.

TABLE F-15
Pilot-Plant Fluorination of Magnesium Fluoride Slag

Run Number	Slag Feed Rate, lb./hr.	Residence Time, hours	Fluorine Concentration, %	Uranium In Residue, Wt. %	Size Fraction	Uranium In Segment, Wt. %	Portion Of Sample, %
1	25.0	1.0	85	0.35	+ 100	0.34	2.9
					- 100 + 200	0.47	8.6
					- 200 + 325	0.31	12.9
					- 325	0.34	75.6
2	18.5	0.9	85	0.19	+ 100	0.39	8.7
					- 100 + 200	0.20	18.3
					- 200 + 325	0.29	8.2
					- 325	0.15	64.8
3	35.5	1.7	85	0.23	+ 100	0.52	1.6
					- 100 + 200	0.39	14.3
					- 200 + 325	0.13	11.7
					- 325	0.19	72.4
4	42.0	0.8	85	0.30	+ 100	0.32	3.3
					- 100 + 200	0.37	29.1
					- 200 + 325	0.28	37.4
					- 325	0.28	30.1
5	42.0	0.8	45	0.33	+ 100	0.41	2.1
					- 100 + 200	0.41	19.9
					- 200 + 325	0.37	25.2
					- 325	0.28	52.8

Leaching tests, using both nitric acid and a mixture of potassium chlorate and sulfuric acid, were run on a minus 200 plus 325 mesh segment of the feed material and on the product from the second tray run. The acid leaches reduced the uranium contents to 0.25 and 0.31%, respectively, which are approximately the same values obtained with tray fluorination. The leaching of the product from run 2 removed an additional 0.05 and 0.06%, respectively, of the uranium contained in the sample. In view of these results, the vibrating-tray fluorination method of uranium recovery appears only slightly less efficient than the wet leaching method, provided the slag is not completely dissolved.

OCTOBER 1, 1957, THROUGH DECEMBER 31, 1957

FLUID-BED HYDROFLUORINATION

A series of tests was performed with a feed of Port Hope oxide to determine the minimum agitator speed required to maintain fluidization in the hydrofluorination reactor. The unit was operated with a feed rate of 45 to 50 pounds of uranium dioxide per hour per cubic foot of bed, reactor wall temperatures of 550 and 850°F. for the first and second stages, respectively, and an overall hydrogen fluoride excess of about 2%. A mixture of 50% water-50% hydrogen fluoride was fed to the first stage, and anhydrous hydrogen fluoride was fed to the second stage. In most of the tests, almost complete conversion of the uranium dioxide to uranium tetrafluoride was realized.

The first stage of the unit performed well without agitation, but attempts to operate the second stage in this manner failed due to caking and channeling of the powder bed. It was possible, however, to operate with agitator speeds as low as 5 rpm. The problems encountered in the second stage may have been due to the higher wall temperature, to the use of anhydrous hydrogen fluoride, or to a greater tendency for the more completely converted powder to sinter. Operation of either stage without agitation does not appear desirable, however, as small variations in processing conditions or powder characteristics would probably result in caking.

ORE CONCENTRATE PROCESSING

Anaconda Ammonia-Precipitated Ore. Analyses of the Anaconda acid-leached, ammonia-precipitated ore concentrate processed in the third quarter of 1957 have been completed and are presented in table F-10. As can be seen from these data, about 50% of the molybdenum and vanadium was removed during the reduction-hydrofluorination steps. Removal of the nonvolatile impurities and further reductions of about 80% of the vanadium and 10% of the molybdenum contents of the uranium tetrafluoride were accomplished during the fluorination step.

TABLE F-10
Analysis of Anaconda Ammonia-Precipitated Ore Concentrate and Related Products

Material	Ca	Fe	P	Mg	Mo(1)	Na	S	U	V(1)
Starting Ore	0.09	0.65	0.06	0.23	40	0.09	0.31	69.6	174
UO_2	0.28	0.73	8.00(1)	0.33	23	0.07	1198(1)	79.9	216
UF_4	0.32	0.61	8.00(1)	0.26	16	0.12	435(1)	68.9	109
Fluorination Tower Ash	3.40	12.80		3.60	2			35.5	15
Fluorination Filter Ash	2.38	20.80		2.60	256			8.0	450
UF_6					18			67.2	27

Note: Results are reported as weight percent except as noted.

(1) Results are reported as parts per million.

South African (Rand) Ore. Approximately 500 pounds of uranium hexafluoride has been prepared from South African (Rand) ore concentrate by reduction and hydrofluorination in the fluid-bed pilot plant, followed by fluorination in the 4-inch diameter tower reactor. The concentrate had bulk and packed densities of 1.0 and 1.6 g./cc., respectively, and contained 70.4% uranium 5 ppm. molybdenum, and 12 ppm. vanadium. Other impurities included 0.46% iron, 0.56% calcium 0.04% nitrate, 1.47% ammonia, 0.02% chloride, and 0.13% sulfur.

The ore fluidized well and was very reactive in both the reduction and hydrofluorination steps.

The feed rate to the reduction unit was about 50 pounds of concentrate per hour per cubic foot of bed; however, low bed temperatures in the second stage showed that all the reduction was completed in the first stage, thus indicating that the feed rate could have been at least twice that employed. In the hydrofluorination step, essentially complete conversion of the reduced concentrate to uranium tetrafluoride was obtained in a single-stage with a uranium dioxide feed rate of about 70 pounds per hour per cubic foot of bed, a reactor wall temperature of 550°F., and a hydrogen fluoride excess of 100%. Analyses of the uranium dioxide and of the uranium tetrafluoride showed that essentially no change in the molybdenum or vanadium contents of the ore occurred in the reduction or the hydrofluorination steps.

The fluorination test was made with an average wall temperature of 615°F., a uranium tetrafluoride feed rate of 50 pounds per hour, a fluorine excess of 25%, and a fluorine inlet concentration of about 90%. No operating difficulties were encountered, and approximately 95% of the uranium tetrafluoride was converted to uranium hexafluoride. Only 1 of the 31 pounds of ash was collected in the filter; the uranium contents of the tower ash and the filter ash were about 50% and 3%, respectively. Inspection of the tower showed a small amount of caking in the top section; however, this was probably due to the low reactor wall temperature.

The analytical results on the uranium hexafluoride prepared from the ore concentrate showed an average concentration of 5 ppm. molybdenum and 3 ppm. vanadium on a uranium basis. Although these values are higher than the 1 ppm. specification for cascade feed, it is probable that some of this material could be tolerated, since the impurity content of the present uranium hexafluoride feed is below the specified amount. In addition, it should be noted that use of a higher hydrofluorination temperature than that employed to process this concentrate, i.e., 1100°F. instead of 550°F., would be expected to result in some decontamination of both the molybdenum and vanadium.

Purification by Distillation of Uranium Hexafluoride. Installation of the uranium hexafluoride batch distillation unit has been completed, and tests are in progress. The 2-inch diameter column is packed to a height of approximately 8 feet with Cannon protruded nickel packing (0.24 inch by 0.24 inch). The stillpot has a capacity of approximately 125 pounds of uranium hexafluoride, and the reflux ratio can be varied by adjusting the time cycle of a swinging bucket-type flow splitter.

The flooding velocity for the Cannon packing was determined to be approximately 7,100 pounds of uranium hexafluoride per hour per square foot, which checks closely with the 7,200 pounds per hour per square foot predicted from the curve of Sherwood, et al., as modified by Lobo, et al*. The relationship of pressure drop and estimated boil-up rate data followed approximately the correlation of Reed and Fenske**.

Studies on the separation of molybdenum and vanadium fluorides from uranium hexafluoride prepared from Anaconda acid-leached, ammonia-precipitated ore concentrate were performed with a boil-up rate of about 5,300 pounds per square foot-hour and a reflux ratio of approximately 90 to 1. The concentrations of both vanadium and molybdenum were easily decreased from 27 and 18 ppm., respectively, to approximately 2 ppm. Attempts to reduce these concentrations further to the 1 ppm. specification for cascade feed have thus far been unsuccessful. The presence of compounds of vanadium and molybdenum which are both more and less volatile than uranium hexafluoride is suggested by the fact that the concentrations of these impurities in the stillpot decreases first and then gradually increases as successive product cuts are removed.

Contrary to predictions based on the high boiling points reported for niobium fluoride and tantalum

* Lobo, W. E., Friend, L., Hashmall, F., and Zenz, F., "Limiting Capacity of Dumped Tower Packings", *Trans. Am. Inst. Chem. Engrs., 41,* 693 (1945).

** Reed, T. M., III, and Fenske, M. R., "Hydrodynamics of Liquid Vapor Flow in Packed Distillation Columns", *Ind. Eng. Chem., 42,* 654 (1950).

fluoride, these contaminants appeared in the initial total reflux distillate sample to the extent of approximately 75 ppm. each, while neither was found in the corresponding bottoms sample. Analysis of the starting uranium hexafluoride showed 1.2 ppm. niobium fluoride and less than 1.5 ppm. tantalum fluoride.

Purification Before Fluorination. Bench-scale studies have been made to determine whether the 50 ppm. of molybdenum and 300 ppm. of vanadium present in the Anaconda acid-leached, ammonia-precipitated ore concentrate can be removed by the formation of volatile compounds of these elements prior to fluorination to uranium hexafluoride. The tests, table F-11, involved exposure to one or more gases and single to three successive treatments.

TABLE F-11

Purification of Ammonia-Precipitated Ore Concentrate

Run Number	Reagent			Temperature, °F.			Time, hours			Analytical Results		
	First Treatment	Second Treatment	Third Treatment	First Treatment	Second Treatment	Third Treatment	First Treatment	Second Treatment	Third Treatment	F^-, %	Mo, ppm.	V, ppm.
2138	H_2			1050			2				51	80
2156	H_2			1050			2				31	297
2150	H_2			1050			3				48	300
2166	H_2	Air	H_2	1050	1050	1050	2	3/4	2		37	335
2157	H_2	HF		1050	750		2	1		25.0	24	255
2142	H_2	HF		1050	750		2	2		25.1	27	186
2133	H_2	HF		1050	1100		3	2		24.6	2	14
2151	H_2	HF		1050	1100		3	2		25.2	2	82
2143	H_2	HF	HF	1050	750	1100	2	1	1	24.7	5	70
2136	H_2	HF	HF + H_2	1050	1100	1100	3	2	2	24.9	4	155
2137	H_2	HF	HF + Air	1050	1100	1100	3	2	2	20.3	5	32
2162	H_2	Air	HF + H_2	1050	1050	1100	2	3/4	2	23.6	1	103
2168	H_2	Air	HF + H_2	1050	1050	1100	2	3/4	2	25.2	34	301
2159	H_2	Air	HF	1050	1050	1100	2	3/4	2	16.9	4	36
2210	H_2	HF		1050	1100		2	3			10	105
2154	HF			770			1/2			15.3	3	43
2155	HF			770			1			15.3	3	48
2149	HF			770			2			15.3	1	36
2152	HF	H_2		770	1050		1/4	1/2		4.6	4	61
2127	HF	H_2		770	1050		2	2		0.8	0.3	5
2164	HF	H_2		770	1050		2	2		2.8	1	44
2128	HF	H_2 + HF		770	1050		2	2		20.2	2	12
2130	HF			1100			2-3/4			17.3	26	116
2131	HF	H_2 + HF		1100	1100		3	2		16.1	1	7
2135	HF	H_2	HF	1100	1050	1100	2	3	2	22.8	1	14
2129	HF + Air			1050			2			14.9	24	28
2139	HF + H_2			900			1			15.1	1	17
2140	HF + H_2			900			2			16.1	2	67
2153	HF + H_2			1050			2			18.7	1	50
2148	HF + H_2			1100			1			17.6	1	19
2132	HF + H_2			1100			2			22.9	8	35
2146	HF + H_2			1200			1			15.0	12	(1)
2147	HF + H_2			1200			2			24.6	14	193

(1) Not analyzed.

The results of tests employing reduction with hydrogen followed by hydrofluorination with anhydrous hydrogen fluoride show that (a) reduction with hydrogen alone removed none of the molybdenum or vanadium impurities; (b) hydrofluorination at 750°F. decreased the molybdenum content from 50 to about 25 ppm. and the vanadium from 300 to about 200 ppm.; and (c) hydrofluorination at 1050 to 1100°F. reduced the molybdenum to 1 to 5 ppm. and the vanadium to about 75 ppm. The use of air to reoxidize the concentrate before or during hydrofluorination resulted in a further lowering of the vanadium concentration to about 35 ppm., but was of no benefit in the removal of molybdenum.

Hydrofluorination of the ore before reduction lowered the molybdenum content to 3 ppm. or less, and the vanadium content to about 40 ppm. with contact times as low as 1/2 hour at 770°F. being effective. Reduction of the uranyl fluoride product with hydrogen at 1050°F. did not reduce the impurity content further, but treatment with a mixture of hydrogen and hydrogen fluoride at 1050°F.

decreased the vanadium content to about 12 ppm. Almost equivalent results were obtained with hydrofluorination at 1100°F. followed by reduction in the presence of hydrogen fluoride and by separate reduction and hydrofluorination. Simultaneous reduction and hydrofluorination of the untreated concentrate at reaction temperatures up to 1100°F. reduced the molybdenum content to about 1 ppm. and the vanadium to 17 to 67 ppm. At 1200°F., the amount of purification decreased, possibly as a result of sintering of the oxide in the initial stages of the reaction.

Although successive hydrofluorination-reduction-hydrofluorination treatments resulted in the best decontamination of both the molybdenum and vanadium impurities, operating costs associated with such a process would be prohibitive, and a higher than specification vanadium impurity would still remain. The use of high hydrofluorination temperatures in the processing cycle used normally will give some decontamination, however, and probably decrease the overall cost of purification by distillation.

PROCESSING OF SLIGHTLY ENRICHED OXIDE

Approximately 4,000 pounds of slightly enriched waste oxide was converted to uranium tetrafluoride in the fluid-bed reduction-hydrofluorination pilot plant. The program was initiated to reduce the quantity of elemental fluorine required to convert this material to uranium hexafluoride and thus reduce the unit cost. Oxides of both high and low density obtained from the burning of metal chips and from the calcination of ammonium diuranate precipitates were processed. Operation of the unit with the high density oxide was essentially trouble-free; however, the conversion to uranium tetrafluoride averaged about 70% due to the low reactivity of this material. With the low density material, conversions of 93% and higher were realized, but some difficulties were encountered with poor fluidization in the reduction step.

The 4-inch diameter pilot-plant fluorination tower was operated 65.7 hours to prepare 3,607 pounds of uranium hexafluoride from the slightly enriched oxides. The average conversion of the oxide to uranium hexafluoride was 95%. Production of uranium hexafluoride for this quarter was low due to a lack of fluorine.

RESISTANCE OF RESIN-FILLED GRAPHITE TO HYDROGEN FLUORIDE AZEOTROPE

The operation of the hydrofluorination systems in the feed plants with a 105% hydrogen fluoride excess results in increased chemical costs which are only partially offset by the sale of the 70% by-product acid. Plant-scale tests have indicated that operation with a low acid excess (5 to 10%) or with a recycled hydrogen fluoride azeotrope stream results in little or no loss in conversion and therefore permits more efficient acid usage. The existing Monel condensers in the feed plant will not withstand the corrosive attack of the waste acid at these conditions, however; and if the azeotrope recycle is used, distillation equipment that is resistant to corrosive attack will also be required.

A survey of the types of material that could be employed in heat transfer equipment for use with hydrogen fluoride water solutions of azeotropic concentration (38% hydrogen fluoride) or less indicated that resin-filled graphite should be suitable. Equipment fabricated from material of this type, Karbate 22 and Impervite, has been used for handling dilute hydrochloric acid solutions and is available at a reasonable cost. Although the manufacturers of Karbate (National Carbon Company) and Impervite (Fall Industries, Inc.) recommended the materials for the hydrofluoric acid service, plant experience was not available. Therefore, test Karbate and Impervite boiler-condenser units were procured from the respective vendors for extensive testing.

The units have shown excellent resistance to boiling and condensing hydrogen fluoride azeotrope.

The Karbate unit was operated at total reflux for 5,088 hours before the test was stopped because of a cracked flange, and the Impervite unit has been in operation for 4,994 hours. The test on Karbate has shown that, for the period studied, (a) the heat transfer surfaces are exceptionally resistant to corrosive and erosive attack by the azeotrope; (b) the heat transfer properties are good as the still was operated at heat fluxes of about 28,000 Btu./hr.-sq.ft., and overall heat transfer coefficients of 510 and 170 Btu./hr.-sq.ft.-°F. were obtained in the boiler and condenser, respectively; (c) with the exception of some porosity noted in the flanges, the material is nonpervious, and closures using Teflon gaskets are effective for containment of the acid; (d) porosity leaks tend to seal themselves as operation is continued; (e) no loss in tensile or compressive strengths due to acid exposure occurs; and (f) as indicated by the low fluoride content (0.16 to 0.24%), the material is relatively unattacked by the hydrogen fluoride.

The test supports the vendor's contention that Karbate 22 will perform satisfactorily in use with hydrogen fluoride azeotrope at operating temperatures up to 300°F. Lower concentrations of acid should be even less destructive to this material. The Impervite unit is smaller than the Karbate unit, and heat transfer and erosion characteristics of the test are not so rigorous; however, no attack has been noted, and since Karbate and Impervite are similar in composition, it is tentatively concluded that Impervite should also be acceptable for service with low acid concentrations.

LABORATORY THERMOBALANCE STUDIES

Activation of Hanford Continuous-Calciner Uranium Trioxide with Ammonia. Recent experience at the Port Hope Refinery, the National Lead Company of Ohio, and the Mallinckrodt Chemical Works has indicated that the addition of ammonia to uranyl nitrate solutions before concentration to uranyl nitrate hexahydrate has materially reduced corrosion of the evaporators. Furthermore, it has been observed that this treatment is apparently responsible for an increase in the reactivity of uranium trioxide which is subsequently produced by pot denitration. Because of the anticorrosion benefits to be gained by ammonia addition and the present difficulty with corrosion in the hydrofluorination facilities of the Paducah feed plant due to the high sulfur content of Hanford oxides, eleven experimental samples or uranium trioxide were prepared by continuous calcination at Hanford to determine the effect of ammonia addition on the reactivity of this type material. Some of the oxides were produced in the 16-inch pilot-plant unit, while others were prepared in the 3-inch diameter laboratory unit.

The hydrogen reduction rates at 1040°F. and hydrofluorination rates at 770°F., determined in the laboratory thermobalance, table F-12, show that an addition of about 2.0% ammonia results in no improvement in reduction and about a 12% improvement in hydrofluorination reactivity when compared to test samples containing no additives. The improvement is about 30% when compared to a test sample evaluated earlier. The addition of 250 ppm. sulfur with about 2.0% ammonia results in a further improvement; and when the sulfur addition was increased to 600 ppm., the hydrofluorination reactivity was essentially the same as that for a test sample prepared by the addition of 3,000 ppm. sulfur alone. A further increase in reactivity was shown by a sample to which 3,000 ppm. sulfur and about 2.0% ammonia had been added during preparation.

It should be noted that the reduction rates for the oxides containing ammonia were quite slow at a temperature of 1040°F. At 1110°F., however, a marked increase in the reduction rate for the sample containing 600 ppm. of sulfur was observed, and the subsequent hydrofluorination rate was not affected adversely.

South African (Rand) Ore Concentrate. Rand uranium ore concentrate is a very reactive material which can readily be converted to uranium tetrafluoride. Complete reduction of a 0.5-gram thermobalance sample was accomplished in 10 minutes at 1040°F. Subsequent hydrofluorination of the uranium dioxide resulted in complete conversion to uranium tetrafluoride in 10 minutes at 770°F.

Continued hydrofluorination removed some of the silicon impurity by vaporization of silicon tetrafluoride. At these processing temperatures, some tendency to sinter was noted, but this characteristic was slight compared to the complete fusion of several other ore concentrates evaluated previously. Since this material is ammonia-precipitated, the observed similarity of its properties and reaction behavior to those of purified ammonia precipitates was not unexpected.

TABLE F-12

Thermobalance Evaluation of Experimental Continuously Calcined Uranium Trioxides

Sample Number	Sulfur Added, ppm.	Ammonia Added, ppm.	Time For Reduction At 1040°F., min.	Time to Attain Indicated Conversion To UF_4 At 770°F., min. 0.80	0.90	0.95	0.98	Conversion To UF_4 After 180 Minutes, wt. %
SHS-18(3)	0	0	60					54.0
5(1)	0	0	50					72.5
6(1)	0	18,000	45					72.7
4(1)	0	19,000	35	140				84.0
SHS-19(2)	0	24,000	45	120				84.3
7(1)	250	20,000	50	80	152			91.8
SHS-20(2)	250	24,000	50	27	55	87	125	
SHS-22(2)	600	17,000	45	17	35	57	100	
SHS-21(2)	600	17,000	18(4)	18	32	55	80	
SHS-21(2)	600	17,000	45	15	32	50	78	
3(1)	3,000	7,600	15	8.0	23	50	137	
1(1)	3,000	0	15	7.5	21	50	133	
2(1)	3,000	18,000	15	7.0	15	28	55	

Note: Samples are listed in order of increasing activity towards hydrogen fluoride based on (1) conversion after 180 minutes if 0.95 conversion was not reached, or (2) time required to reach the 0.95 level.

(1) Prepared in 3-inch diameter reactor.
(2) Prepared in 16-inch diameter reactor.
(3) A pilot-plant sample with no added sulfur or ammonia evaluated earlier.
(4) Sample reduced at 1110°F.

JANUARY 1, 1958, THROUGH MARCH 31, 1958

ORE CONCENTRATE PROCESSING

In the existing process for the conversion of impure ore concentrates to uranium hexafluoride, the costs of preparing pure uranium trioxide from the concentrate and converting this material to uranium hexafluoride are essentially equal. Large economic gains are potentially available, therefore, if the process could be modified to allow direct handling of the concentrates in the cascade feed plants, thereby eliminating the costly purification and denitration operations. Accordingly, an experimental program is being carried out to develop methods of processing this material and to determine the extent to which existing equipment can be utilized. The results of all studies to date are reviewed below, along with the presentation of the accomplishments in the last quarter.

Types of Concentrates

At the present time, the ore concentrates fall into two general categories: These are (a) the relatively pure ammonia precipitates; and (b) the sodium or magnesium salts which represent about 75% of the available concentrates and normally assay 5 to 10% metallic impurities (primarily, the precipitating agent). Both classes of material contain varying amounts of molybdenum and vanadium which form volatile compounds in the fluorination step and are collected along with the uranium hexafluoride.

The concentrates which have been studied appear in table F-15 along with pertinent analytical data.

TABLE F-15
Ore Concentrate Analyses

	U, %	Na, %	Mg, %	Other Metals, %	S, %	Mo, ppm.	V, ppm.	Bulk Density, g./cc.	Packed Density, g./cc.
Anaconda Acid Leach (Two Batches)	69	0.1	0.5	2.5	1.0	27	175	0.7	1.2
Anaconda Carbonate Leach	61	7.4	0.06	1.5	0.05	2.5	2000	0.9	1.5
Anaconda Carbonate Leach	62	2.3	3.7	3.5	0.07	6	340	0.5	0.8
South African Rand Ore	74	0.05	0.05	1.2	1.4	5	12	1.0	1.6

Previous Work

Reduction-Hydrofluorination. All materials noted have been reduced in the 6-inch diameter, two-stage fluid-bed unit and hydrofluorinated in the 6-inch diameter, two-stage stirred fluid bed or in the 15-foot long pilot-plant vibrating tray. Unlike the approach at Argonne, the concentrates were handled as fine powders, and special granulating before processing was not required. Although the materials were considerably less dense than most purified oxides currently being processed in the feed plants, they were very reactive, and it was possible to obtain throughput rates and conversions comparable to those realized with the dense oxides. This is not too surprising with the ammonia concentrates, since previous work with oxides made from ammonium diuranate would have predicted good results. It is felt that the success with the sodium-bearing materials, however, was largely due to low temperature hydrofluorination; caking was discouraged, since bed temperatures never reached the point at which $NaF \cdot UF_4$ would sinter and cause trouble.

Fluorination. In the fluorination step, the uranium tetrafluoride derived from ammonium diuranate processed well through the 4-inch diameter pilot-plant flame reactor, and no difficulties in plant operation are anticipated. With sodium-bearing uranium tetrafluoride, however, severe caking on the tower walls was observed. It is evident from these tests that tower fluorination, employing the present reactor design, is impractical if the sodium content of the feed is high.

Purification. Purification by distillation appears uncomplicated. Pilot-plant tests show the presence of molybdenum and vanadium compounds in the uranium hexafluoride and both appear as high and low boiling impurities. This information is in direct contradiction with Argonne results on "spiked" samples where only low boilers were observed; thus, it appears that the fluorination method will determine the nature and form in which impurities occur. Based on engineering calculations, two columns each with forty theoretical plates should be adequate to obtain satisfactory product purity.

Present Program

With respect to ammonia concentrates, no additional pilot-plant effort through the fluorination step is planned, since it is felt that all necessary work, short of plant tests, has been completed. Use of existing equipment for the fluorination of high sodium concentrates poses a serious problem, however, and significant additional chemical costs would be required in the hydrofluorination step to form the fluorides of the metallic impurities. It is obvious, therefore, that the best approach to the problem would be to develop a method for sodium and magnesium elimination prior to hydrofluorination. Simple leaching treatments of the concentrate or of the oxide after reduction appear promising and are discussed in detail below.

Development emphasis is also being placed on simplification of the uranium hexafluoride purification step. Laboratory and bench-scale tests have already shown that the concentrations of molybdenum and vanadium can be reduced significantly in the hydrofluorination step. In addition, preliminary studies indicate that essentially complete removal of vanadium from uranium hexafluoride can be achieved by selective sorption in beds of Monel wool, fused alumina, or sodium fluoride.

In case the methods outlined above are not developed successfully, experimental studies are being made to determine if the high sodium material can be fluorinated in a fluid-bed reactor. Use of such a unit for processing of feed plant ash containing a large percentage of impurities might also be feasible.

Removal of Sodium and Magnesium. The initial attempts to reduce the sodium and magnesium contents of ore concentrate involved a water wash of the reduced oxide. The results of tests with concentrate containing 2.3% sodium and 3.7% magnesium, table F-16, showed that a large portion of the sodium, but little of the magnesium, could be removed by this treatment. It can also be seen that the amount of sodium retained in the oxide decreased as the reduction temperature was increased. At the highest temperature, which is practical from a production standpoint, 1200°F., the sodium content was reduced to 0.5%.

There appears to be two possible reasons for the effect of reduction temperature on the effectiveness of the water wash. As the reduction temperature increases, the surface area of the oxide is decreased, and there is less tendency for reoxidation. Also, there will be less sodium absorbed

on the powder. Both possibilities are supported by the facts that no sodium can be washed from completely reoxidized powder and that pure oxide which has been prepared at a low temperature will retain about 0.2% sodium when it is washed with a sodium hydroxide solution.

TABLE F-16

Effect of Water Leaching on Sodium and Magnesium Contents of Ore Concentrates Reduced at Various Temperatures

Reduction Temperature, °F.	Nitrogen Surface Area, sq.m./g.	Sodium, %	Magnesium, %
Starting Material		2.30	3.70
1050	12.2	0.90	
1100		0.85	
1200	6.5	0.50	3.25
1400		0.55	
1700	2.2	0.30	3.28

In an attempt to reduce the impurity content further, oxides reduced at 1200°F. were washed and then leached with solutions of various compounds. Acid leaches usually dissolved some uranium and, with the exception of oxalic acid, were not particularly effective in reducing the sodium or magnesium contents. With ammonia salts, however, sodium and magnesium concentrations of 0.25 and 1.2%, respectively, were obtained consistently with values as low as 0.10 and 0.40 being noted. About 0.2 pound of ammonium chloride or 0.4 pound of ammonium sulfate per pound of uranium was adequate. On this basis, the chemical cost per pound of uranium would be about $0.012 for ammonium chloride and $0.010 for ammonium sulfate.

In view of the success with the ammonia salts, similar tests were made with unreduced ore concentrate. In general, the results were equivalent to those obtained with the reduced oxide. This latter method would probably be preferred for production use, since the ore treatment facilities need not be connected directly to the existing reduction equipment. The treated powders must be evaluated with respect to reactivity and processing characteristics, however, before a choice can be made.

It is planned to optimize the leaching conditions for the concentrate described above, and to obtain other ores for additional studies.

Removal of Vanadium and Molybdenum from Uranium Hexafluoride by Selective Sorption. A series of experiments has been conducted to determine if vanadium and molybdenum impurities in uranium hexafluoride prepared from ore concentrate can be removed by vaporizing the uranium hexafluoride through a bed of sorbent. Tests were made with sodium fluoride, fused alumina, Drierite, activated alumina, and Monel wool, which were packed to a depth of 6 inches in a 3-inch Monel pipe and treated with elemental fluorine before use. A boiling water bath was employed to vaporize impure uranium hexafluoride through each bed in successive charges of approximately 100 grams each at a velocity of about 0.5 to 1.0 foot per minute. The effluent uranium hexafluoride was collected in a pair of series-connected cold traps immersed in a dry ice bath. All experiments except that with sodium fluoride were conducted at 300°F. with the system evacuated and dead-ended. To avoid reaction of uranium hexafluoride with sodium fluoride, the bed was held at 750°F., a fluorine bleed of approximately 10 mol percent was employed, and the exit gas was vented through the cold traps to an alumina trap. In each experiment, the final step was treatment of the bed with fluorine to drive off any uranium compounds retained in the sorbent.

Analyses of the uranium hexafluoride collected in the cold traps showed that the vanadium was

removed almost completely by all of the materials noted. Uranium hexafluoride charges containing 17 and 70 ppm. vanadium were used, and the impurity concentration was reduced to less than 1 ppm. Extremely high vanadium concentrations, up to 870 ppm., in the residue from the vaporizers indicated that as much as 40% of the vanadium in the feed may have reacted with the Monel metal in the cylinders. At least partial desorption of the vanadium on fluorination of the sodium fluoride, fused alumina, and Drierite was observed. Data are not yet available on the fluorination effluent for activated alumina and Monel wool.

Molybdenum was retained on fused alumina, activated alumina, Drierite, or Monel wool. The concentration in the uranium hexafluoride was reduced from 22 and 8 ppm. to approximately 15 and 4 ppm., respectively. In the case of sodium fluoride, however, no decrease was noted in the effluent uranium hexafluoride. Partial desorption of the molybdenum during fluorination of Drierite and fused alumina was observed.

It is planned to continue the studies and to determine the effect of increasing the depth of the sorbent bed. Tests will also be made with other materials.

Purification by Distillation of Uranium Hexafluoride. Additional studies on the separation of molybdenum and vanadium fluorides from uranium hexafluoride prepared from Anaconda acid-leached, ammonia-precipitated ore concentrates were performed in the batch distillation column described previously . In several instances, the concentrations of these impurities were reduced below the maximum of 1 ppm. specified for cascade feed, but the results were not consistent. The erratic nature of the data might be the result of sorption of vanadium and molybdenum compounds on the nickel packing or on the Monel pipe employed in the still and sampling cylinders. This theory is suggested by the fact that it was possible to account for only 50% of the vanadium and 70% of the molybdenum charged to the still. Further support is lent to this hypothesis by the fact that a sizeable proportion, up to 40%, of the vanadium initially present in a Monel sample tube remained in the residue when better than 99% of the uranium hexafluoride was vaporized from the cylinder. The enrichment in molybdenum was much less pronounced; only 4% of the initial quantity remained in the residue.

The inconsistent results encountered in the course of the distillation studies do not prevent the drawing of some general conclusions from the data. Additional evidence was obtained to support the previously reported suggestion that compounds of molybdenum which are both more and less volatile than uranium hexafluoride are obtained when ore concentrate is fluorinated. As successive product cuts were distilled off, the molybdenum in the stillpot concentration decreased from 18 ppm .to as low as 1.9 ppm., and then increased to 20 ppm. Samples drawn at total reflux upon completion of the run showed an enrichment ratio for the top of the column of 0.5, thus indicating the presence of a molybdenum compound less volatile than uranium hexafluoride.

Distillation studies will be discontinued until the evaluation of other purification methods is completed.

Fluid-Bed Fluorination. The fluid-bed fluorination studies were made in an existing reactor, 6 inches in diameter with a 30-inch bed depth, which was fitted with a removable mechanical stirrer so that tests could be performed with and without externally supplied agitation. The reactor was heated with beaded Nichrome wire resistance elements, and no direct cooling was provided. Mixtures of fluorine and air in the desired concentrations were introduced into the reactor through a perforated metal bed support. Sintered metal filters removed the entrained dust from the off-gases, and the uranium hexafluoride formed in the reaction was recovered by cold trapping.

As an aid to fluidization, the uranium tetrafluoride was blended with magnesium fluoride. For the first three tests, crude uranium tetrafluoride prepared from ore concentrate containing 2.3% sodium and 3.7% magnesium was blended with minus 40-mesh magnesium fluoride slag; for the remainder of the studies, a more closely sized slag, i.e., minus 40, plus 200-mesh, was used. Mechanical stirring was employed in the initial tests, but the fluidizing characteristics of the blended powders were found to be good, and the use of the stirrer was discontinued after the third run.

The crude uranium tetrafluoride content of the blended feed powder was varied from 50 to 80% with satisfactory mechanical operation over the entire range. The maximum rate of conversion to uranium hexafluoride, 36 pounds of uranium per hour per cubic foot of bed, was obtained with 20% magnesium fluoride, a fluidizing velocity of 1.1 foot per second (27% fluorine-73% air), and a bed temperature of 1050°F. About 86% of the uranium fed was converted to uranium hexafluoride. An insufficient supply of crude uranium tetrafluoride prevented testing of the reactor at higher rates with the impure feed.

Additional capacity studies were made with a high density uranium tetrafluoride prepared from a Hanford continuous-calciner oxide. A maximum fluorination rate equivalent to 77 pounds of uranium per hour per cubic foot of bed was obtained with a solids feed of 95% uranium tetrafluoride and 5% magnesium fluoride, a bed temperature of 1045°F., and an inlet fluorine concentration of 45%. It should be noted that, although no attempt was made to optimize the conversion efficiency of the uranium tetrafluoride to uranium hexafluoride reaction, values as high as 94% were obtained.

For all of the tests, cooling could be obtained only by removing the insulation from the reactor. It appears probable, therefore, that the maximum rates noted above could be increased if forced cooling were employed.

For a system employing magnesium fluoride diluent, recycling of a portion of the solids discharged would be necessary to minimize the amount of material requiring additional processing for complete uranium removal. It would also be desirable, and perhaps necessary, to remove the greater portion of the sodium fluoride from the recycle stream to maintain a low concentration of this material in the fluid bed. High concentrations of sodium fluoride might result in caking and/or poor fluidization.

Examination of the solid residues from the fluorination test runs with the crude uranium tetrafluoride feed showed that the sodium fluoride waste was preferentially removed from the ash by screening through a 200-mesh sieve. In general, sodium concentration factors ranging from 2 to 7 were obtained. From the above results, it appears probable that no difficulty would be met with maintaining a low sodium concentration in the recycle magnesium fluoride.

From 60 to 75% of the magnesium fluoride was found to be reclaimable by this screening. It is expected, however, that the losses due to attrition would decrease upon repeated recycling, since the more friable particles would be removed in the initial few cycles. A study to determine the extent of the losses upon repeated recycling would be necessary, however, to make an accurate estimate of the required make-up rate.

No further work on fluid-bed fluorination is planned unless the purification studies described above are unsuccessful and the standard flame reactors cannot be used to process ore concentrates.

ACTIVATION OF HANFORD CONTINUOUS-CALCINER OXIDE WITH AMMONIA

Recent experience at the Port Hope Refinery, the National Lead Company of Ohio, and the Mallinckrodt Chemical Works has indicated that the addition of ammonia to uranyl nitrate solution increases the reactivity of the uranium trioxide which is produced by pot denitration of this material. To

determine if a similar beneficial effect could be noted with continuous-calciner oxide, Hanford was requested to prepare samples containing about 2% ammonia for evaluation at the Oak Ridge Gaseous Diffusion Plant. Some of the oxides were prepared in the 16-inch pilot-plant unit, while others were produced in the 3-inch diameter laboratory reactor. In the preparation of the samples, the amount of sulfuric acid added before denitration was varied to give sulfur contents ranging from zero to 3,000 ppm. on a uranium trioxide basis. This was done to determine if the activation effects of both treatments were additive.

The reduction and hydrofluorination rates determined in the laboratory thermobalance show that an addition of about 2.0% ammonia results in no improvement in reduction and about a 12% improvement in hydrofluorination reactivity when compared to test samples containing no additives. The addition of 250 ppm. sulfur with about 2.0% ammonia results in a further improvement; and when the sulfur addition was increased to 600 ppm., the hydrofluorination reactivity was essentially the same as that for a test sample prepared by the addition of 3,000 ppm. sulfur alone. A further increase in reactivity was shown by a sample to which 3,000 ppm. sulfur and about 2.0% ammonia had been added during preparation. The reduction rates for the oxides containing ammonia were quite slow at a temperature of 1040°F. At 1110°F., however, a marked increase in the reduction rate for the sample containing 600 ppm. sulfur was observed, and the subsequent hydrofluorination rate was not affected adversely.

Two batches of this material containing 2% ammonia and 250 and 600 ppm. sulfur were evaluated in the fluid-bed reduction-hydrofluorination pilot plant. In the tests with the oxide containing 250 ppm .sulfur, repeated caking occurred in the first stage of the reduction reactor, and no hydrofluorination studies were made. Attempts to prevent the caking by employing high fluidizing velocities and by batch reducing until a bed of uranium dioxide was established in the reactor were unsuccessful. The lack of success can probably be explained by the fact that the reduction rate of this material is about one-fifth that of most of the oxides employed in the feed plants. The flow properties of the powder also seemed to be poor.

Good operation of the pilot-plant unit was obtained with the oxide containing 600 ppm. sulfur. Increasing the reduction temperature to 1110°F. compensated for the slow reduction rate, and the material appeared quite reactive in the hydrofluorination tests. The conversion to uranium tetrafluoride was about 96%, as compared to the 94% obtained previously with oxides containing 1,600 ppm. sulfur only.

APRIL 1, 1958, THROUGH JUNE 30, 1958

The previously described experimental program aimed at the development of methods of processing ore concentrates directly in the cascade feed plants was continued. The studies were concerned primarily with the investigation of (1) techniques of leaching sodium and vanadium from Monticello ore concentrate, and (2) the use of solid sorbents for the removal of molybdenum and vanadium from impure uranium hexafluoride. In addition, several fluid-bed fluorination tests were made to determine the capacity and efficiency of a steam-cooled reactor.

LEACHING TESTS

Studies are being made to determine the effectiveness of various leaching treatments for the removal of sodium from Monticello ore concentrate. This material has bulk and packed densities of 0.7 and 1.3 g./cc., respectively, and according to the official assayer, contains 66% urano-uranic oxide, 4.2% vanadium pentoxide, and9.3% sodium. Other major impurities noted are 1.2% calcium, 0.5% iron, 0.2% copper, 3.9% carbonate, and 0.3% sulfate. Analyses at the Oak Ridge Gaseous Diffusion Plant, however, show a lower sodium content, 7.5%, and 8.4% silicon dioxide. The concentrate is apparently prepared by caustic precipitation from a sodium carbonate solution.

In the leaching tests, a water to solids ratio of 3.3 to 1 was employed, and the slurry was agitated vigorously for 30 minutes at 200°F. before filtering. It was found that three successive treatments using an addition of 0.33 pound of ammonium sulfate per pound of concentrate reduced the sodium content to 0.20%; with one-half the additive, a slightly higher sodium concentration of 0.30% was obtained. Only 40% of the sodium was removed by two washes with water. Studies to determine the optimum leaching conditions showed that, in general, sodium removal was increased by the use of higher temperatures and a pH of about 6.0. Essentially none of the contaminants, other than sodium, were removed by the above treatment.

The presence of soluble carbonate in the concentrate apparently results in the solution of a small quantity of uranium during the washing procedure. Bench-scale tests indicate that the quantity of uranium in the filtrate from the initial wash can be minimized by controlling the pH to about 6.0; the solubility is increased from about 60 ppm. uranium in the filtrate at a pH of 6.0 to 1,260 ppm. at a pH of 8.9. Based on the water to concentrate ratio of 3.3 to 1, a uranium loss of about 0.04% would be expected when operating with the lower pH. Efforts to reduce this loss further by acidification to remove carbonate followed by precipitation with ammonium hydroxide to recover the soluble uranium will be made.

In the bench-scale washing experiments, the vanadium content of the concentrate was not reduced appreciably by the standard ammonium sulfate washing treatment; however, reduction with hydrogen followed by slurrying twice in water removed about 95% of this contaminant. The sodium content of the dried oxide product was 1.2%. Slurrying first in water and then reslurrying in an ammonium sulfate solution decreased the sodium concentration to 0.3%. The above tests indicate that both vanadium and sodium can be removed by the leaching treatment if the ore is reduced first.

A study was also made to determine the feasibility of recycling the filtrates to minimize ammonium sulfate usage. Possible conditions were simulated by adding sodium sulfate or sodium hydroxide

to the original slurry along with the ammonium sulfate and then reslurrying with water. The data presented in table F-10 indicate that sodium as sodium sulfate would not interfere appreciably with recycling, but that sodium as sodium hydroxide decreases the wash effectiveness considerably. From these results, it appears that the sodium removal mechanism involves the metathesis of ammonium sulfate with sodium hydroxide or other base to form a sulfate salt and ammonium hydroxide which is decomposed at the close to boiling temperature of the slurries to evolve ammonia gas and water.

TABLE F-10
Effect of Added Sodium Sulfate or Sodium Hydroxide on Leaching of Sodium from Monticello Concentrate

Run Number	$(NH_4)_2SO_4$, lb./lb. of Concentrate	Na_2SO_4, lb./lb. of Concentrate	NaOH, lb./lb. of Concentrate	Na in Washed Concentrate, %
1	0.33	0	0	1.7
2	0.33	0.06	0	2.2
3	0.33	0.10	0	2.2
4	0.33	0.17	0	1.9
5	0.33	0.23	0	2.3
6	0.33	0	0.06	3.7
7	0.33	0	0.17	5.2
8	0.33	0	0.23	6.2

A pilot plant for larger scale purification of high sodium ore concentrates has been completed, and preliminary tests are in progress. The plant consists of two agitated slurry tanks, a continuous rotary vacuum filter, and the necessary auxiliary equipment. Prior to testing in the fluid-bed reduction-hydrofluorination pilot plant, the processed filter cake will be dried in the vibrating-tray furnace muffle.

THERMOGRAVIMETRIC EVALUATION OF THE FEED PROPERTIES OF AMMONIUM SULFATE LEACHED MONTICELLO URANIUM ORE CONCENTRATE

Thermogravimetric data obtained with the thermobalance described previously* demonstrated that Monticello uranium ore concentrate, after being leached with ammonium sulfate to decrease the sodium content, is a comparatively reactive material. Reduction in hydrogen at 930°F. was complete in 20 minutes, which is approximately the time required to reduce a composite sample of recent Hanford continuously calcined oxides. At 770°F., more than 95% of the contained uranium in the reduced product from the ore concentrate was converted to uranium tetrafluoride in 10 minutes, as compared to the 47 minutes required for the same conversion of the reduced Hanford oxide. To obtain this estimate of conversion, it was necessary to calculate the contained uranium from thermogravimetric hydrolysis data of the completely hydrofluorinated product. The difference between the weight after hydrolysis and that following the initial reduction was assumed to be silicon dioxide, which was lost as silicon tetrafluoride during hydrofluorination. On this basis, the silicon content of the leached ore concentrate, calculated as silicon dioxide, was 8.7% by weight; a value of 9.2% was found by chemical analysis. Spectrographic analyses of the materials before and after conversion to uranium tetrafluoride in the thermobalance showed that the silicon was the only metallic impurity volatilized under the reaction conditions employed, although the ore concentrate contained approximately 2% vanadium.

* Orrick, N. C., Jones, C. G., and Rapp, K. E., *Oxygen Enrichment of Uranium Dioxide and Its Effect Upon Hydrofluorination Reactivity*, Union Carbide Nuclear Company, Oak Ridge Gaseous Diffusion Plant, January 21, 1958 (K-1359).

PURIFICATION OF ORE CONCENTRATE
URANIUM HEXAFLUORIDE

As reported previously , emphasis is being placed on the development of a simple purification step as an alternate to distillation for the removal of vanadium and molybdenum fluorides from uranium hexafluoride which was prepared directly from ore concentrate. Laboratory scale tests had shown that these contaminants are removed selectively when the impure uranium hexafluoride is vaporized through fixed beds of sorbents, such as aluminum fluoride, calcium fluoride, and Monel wool. Since installation of a bed of one of these solid materials between the vaporizers and the cascade could provide the simple purification step desired, a pilot plant has been constructed to study the dynamics of the sorption. The unit consists of a 7-foot long, 3-inch diameter pipe with the necessary feeding, sampling, and trapping systems.

Approximately 100 pounds of uranium hexafluoride was vaporized at a rate of 4 to 6 pounds per hour through each of three sorbents, calcium fluoride (surface area 3 sq.m./g.), fluorinated alumina* (surface area 11 sq.m./g.), and Monel wool. Bed heights were 1.5, 3.0, and 4.0 feet, respectively. Analyses of the outlet gas from the calcium fluoride bed, table F-11, show that, with a bed temperature of 300°F., approximately 98% of the vanadium and 30% of the molybdenum in the feed were removed initially, and that the stripping efficiency for both contaminants decreased to essentially zero after 7 hours of operation. The amounts of vanadium and molybdenum removed from the uranium hexafluoride by the calcium fluoride were determined by difference to be, respectively, 127 and 15.5 mg. per pound of calcium fluoride. Material balances indicate that uranium pick-up by the bed was negligible.

TABLE F-11
Sorption of Molybdenum and Vanadium from Uranium Hexafluoride by Calcium Fluoride

Onstream Time, hours	Mo In Feed, ppm.	Mo In Effluent, ppm.	V In Feed, ppm.	V In Effluent, ppm.
1	22.9	16.2	95.0	1.5
4		14.3		57.0
7		14.5		175.0
9	12.7	12.1	107.0	119.0

Under similar operating conditions, use of fluorinated alumina reduced the molybdenum concentration from approximately 4 ppm. to about 1 ppm., table F-12. Because of the unexplained variation in the vanadium concentration of the feed, the effectiveness of the sorption of this contaminant is indicated only generally by the fact that most of the analyses on the effluent uranium hexafluoride show vanadium concentrations which approach the specification level of 1 ppm. The quantities of vanadium and molybdenum transferred to the aluminum fluoride were estimated to be 43 and 20 mg. per pound of aluminum fluoride, respectively. The uranium retained by the bed was insignificant. Assuming a linear equilibrium and employing the method of Hougen and Watson, the height of a transfer unit for molybdenum has been estimated to be 2.8 feet.

Monel wool removed little of either impurity, although bench-scale tests had indicated good initial removal. Thus, it appears that either the capacity of the wool or the rate of sorption after a brief initial period is too low to warrant further investigation.

* Lengthy pretreatment of the alumina with elemental fluorine had converted about 7% of the material to alumium fluoride.

TABLE F-12

Sorption of Molybdenum and Vanadium from Uranium Hexafluoride by Aluminum Fluoride

Onstream Time, hours	Cumulative UF_6 Fed, lbs.	Mo In Feed*, ppm.	Mo In Effluent*, ppm.	V In Feed*, ppm.	V In Effluent*, ppm.
0.5	2.5	4.2	0.5	7.4	0.5
2.5	13.8	4.1	0.9	8.6	0.8
4.5	24.8	3.5	0.2	8.9	0.5
6.5	35.9	3.8	1.2	7.3	1.0
8.5	47.0	3.9	0.8	15.0	0.5
10.5	58.0	3.5	1.0	22.1	5.2
12.5	69.0	3.6	1.4	14.3	1.2
14.9	82.3	2.4	1.6	13.0	0.6
17.5	96.6	3.1	1.6	5.3	0.5
20.0	110.5		1.7		2.6
Unit was shut down for 4 weeks before resuming operation.					
22.25	125.0	2.6	1.1	12.5	17.7
24.25	138.0	2.9	0.5	7.3	9.6
26.25	151.0	3.5	0.7	5.7	2.7
28.25	164.0	4.7	0.5	8.0	1.5
28.90	170.0	4.3		5.1	
30.00	172.0	5.0		6.8	

* Reported on a uranium hexafluoride basis.

The same uranium hexafluoride feed cylinder was employed for the three sorption runs described above. Drastic reductions in average concentrations of 107 to 30 to 8 ppm. vanadium and 25 to 6 to 4 ppm. molybdenum were experienced from run to run. These changes cannot be explained by assuming a simple distillation effect. Explanations for, and possible applications of, this phenomenon are being sought.

Additional sorbents, magnesium fluoride and copper wool, were evaluated in the bench-scale equipment. Vanadium and molybdenum were preferentially removed by both sorbents, but their capacities appeared extremely low.

Further studies will place emphasis on sorptive capacity. Aluminum fluoride and calcium fluoride materials which have greater surface areas, 40 and 17 sq.m./g., respectively, have been prepared by fluorination of 8 to 16-mesh alumina and 6 to 8-mesh calcium sulfate. Effect of inlet concentration on the effluent purity and bed capacity, as well as the feasibility of absorbent regeneration, will be investigated.

FLUID-BED FLUORINATION

Fluid-bed fluorination studies made previously indicated that forced cooling of the reactor would be necessary to attain high processing rates. The 6-inch diameter pilot plant unit was modified, therefore, by continuously welding a cooling coil to the reactor walls. In addition, the solids feed point was moved from the bottom to several inches above the top of the powder bed to lower the pressure at the screw feeder and thus minimize leakage of fluorine into the uranium tetrafluoride hopper.

Tests with the revised unit show that processing rates of at least 135 pounds of uranium per cubic foot of bed can be obtained with steam cooling. Employing a solids feed of 95% pure uranium tetrafluoride and 5% magnesium fluoride and a fluidizing gas containing about 95% fluorine, the bed temperature was maintained at 1060°F. without difficulty, and greater than 99% of the uranium tetrafluoride was converted to uranium hexafluoride. Inspection of the powder bed upon completion of each of three 3-hour runs at the above conditions showed no evidence of caking.

No further studies with pure uranium tetrafluoride are planned. Higher fluorination rates could probably be obtained if water were used as the coolant, but the capacity of the existing system appears ample for any anticipated production application. Use of this fluorination method will be required only if impurities, such as sodium, which will prevent the use of a tower reactor cannot be removed satisfactorily from the ore concentrates.

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* K-1361 loc. cit.

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The investigation of the feasibility of processing ore concentrates directly in the cascade feed plants was continued. Tests were made to determine the extent to which impurities could be leached from a number of concentrates; the leached materials were evaluated by thermobalance reduction and hydrofluorination tests; the use of solid sorbents to remove the vanadium and molybdenum from uranium hexafluoride was studied further; and processing of Rand (South African) ore concentrate was started in the Paducah feed plant. Work not connected with the ore concentrate problem included large-scale studies of the removal of uranium from magnesium fluoride slag by direct fluorination, preliminary investigations of the possibility of preparing hydrogen fluoride from magnesium fluoride, and a cursory study of gas phase hydrolysis of uranium hexafluoride.

ORE CONCENTRATE PROCESSING

Purification by Leaching. It has been shown by fluorination studies that ore concentrates containing appreciable quantities of sodium cannot be processed in the existing flame reactors. Low melting sodium compounds collect on the tower walls and soon plug the unit. Based on plant operating experience with Hanford oxide received just after start-up of their denitration facility, it is felt that the concentration of this impurity must be lower than 0.3% to eliminate the plugging problem.

Since most ore concentrates contain more than the allowable amount of sodium, the possibility of purification by leaching with solutions of various compounds is being investigated. Previously reported studies had shown that aqueous solutions of ammonium chloride, ammonium nitrate, and ammonium sulfate were equally effective in reducing the sodium content of several concentrates to the desired level. There is a small cost advantage to the use of the sulfate, however, and all recent tests have been made with this material.

The results of bench-scale studies with ore concentrates from eighteen United States and six Canadian ore mills are summarized in table F-14. A water to concentrate to ammonium sulfate ratio of 3.3 to 1 to 0.33 was employed, and the slurry was agitated for 30 minutes at 200°F. before filtering. Each test consisted of either two or three successive treatments. Since the quantity of most of the samples of United States concentrates was too small to permit more than one or two tests, the best leaching conditions could not be determined for each material.

It can be seen from the data that the sodium content of most of the concentrates was either low enough as received or could be reduced satisfactorily by leaching. Although sodium removal was the prime objective of the treatment, about 50% of the magnesium and some calcium were removed. Most of the United States concentrates contained relatively small quantities of magnesium (less than 1%), but four of the Canadian concentrates contained 7% or more. Removal of these contaminants may not be necessary from an operational standpoint, but would result in decreased hydrogen fluoride costs in the hydrofluorination step.

Larger scale leaching studies were made with a Monticello ore concentrate which contained 7-1/2% sodium and 48.1% uranium. The facility employed consisted of two baffled, 40-gallon mixing tanks equipped with turbine-type agitators and a 1-foot wide by 3-foot diameter Oliver rotary vacuum filter.

About 1,000 pounds of concentrate was processed, and it was found that three successive washing treatments, each employing 3 pounds of water and 0.33 pound of ammonium sulfate per pound of concentrate, consistently reduced the sodium content to less than 0.2%. Operation of the system was essentially trouble-free; however, initially the filtration rate was very low, averaging about

2 pounds of dry concentrate per hour per square foot of filter area. In addition, the presence of carbonate, which comprised approximately 3% by weight of the starting concentrate, resulted in the loss of a considerable quantity of uranium. The filtrate had a pH of 9.4 and contained about 1% uranium. Acidification of the slurry to a pH of about 6.5 reduced the uranium content of the filtrate to less than 200 ppm. and had no effect on the filtration rate.

Attempts to increase the filtering rate by decreasing the amount of shear the solid particles were subjected to in the mixing step and by changing the filter cloth from Dynel to Teflon were unsuccessful. Use of a slurry pH of 5.7, however, gave an acceptable filtration rate. With the lower pH, additional uranium was dissolved, and a neutralizing tank and back-up filter would be required for recovery purposes. Such a system would probably be necessary in any event to take care of breaks in the filter cloth and other operational mishaps.

TABLE F-14

Purification of Ore Concentrates by Aqueous Ammonium Sulfate Leaching

	Sodium[a], %			Magnesium[a]			Thermogravimetric Data [b]					
							Reduction		Hydrofluorination			
Concentrate	As Recd.	After Two Slurries	After Three Slurries	As Recd.	After Two Slurries	After Three Slurries	Time To Reach 97% Conv., min.	Time To Reach 100% Conv., min.	Time, min.	Conv., %	Time, min.	Conv. %
Anaconda Acid	3.0	0.4		3.0	1.0		4	13	6	90	30	93
Anaconda Carbonate	12.0	1.4	0.3	0.3	0.2	0.3	9	20	5	62	180	85
Climax Uranium	2.0	0.9	0.8	0.1			65	90	5	49	180	82
Dawn Mining	0.1	0.1		0.2			3	6	5	86	10	87
Durango	3.0	1.9	2.0	0.3	0.2		40[c]		5	23	180	70
Gunnison Mining	7.0	1.0	0.3	0.7		0.1	5	10	2	92	20	98
Homestake NMP	14.0	7.0	3.3				21	35	5	57	75	79
Kerr McGee	3.0	1.1	1.1	4.0	1.9		12	20	5	83	180	98
Lucky Mac Uranium	6.0	1.5	0.5				7	15	5	85	180	91
Mines Development	5.0	0.3		0.3			4	10	5	97	15	100
Monticello Acid	1.0	0.1		1.0	0.5		6	30	3	98		
Monticello Carbonate	17.0	2.0	0.4	0.8	0.6	0.6	7	12	10	85		
Rare Metals	0.2	0.1		1.0	0.3		3	8	3	98		
Rifle	2.0	0.1		0.1	0.1		5	10	6	98		
Texas Zinc Minerals	0.7	0.1		0.1	0.1		5	15	3	98		
Trace Elements	9.0	2.4	2.0	0.3		0.3	12	20	6	92		
Uravan	2.0	0.7	0.3	1.0	0.2		7	25	5	98		
Uranium Reduction	0.1	0.1		0.1	0.1		7	20	3	98		
Vitro Uranium	0.2	0.1		0.1	0.1		13	20	5	95	75	113
Western Nuclear	0.1	0.1		0.1	0.1		4	18	3	79		
Algom	5.0	0.7	0.3	0.2			6	15	5	92	10	93
Can-Met	1.0	0.1	0.3	12.0	3.0		6	20	5	84	10	86
Denison	0.3	0.1	0.1	9.0	2.4	4.4	5	8	5	90	10	94
Faraday	3.0	1.6	1.4	7.0	3.5	4.0	8	20	10	80	90	87
Lorado	3.0	0.6	0.6	7.0	3.3	4.1	7	12	5	80	180	90
Northspan	6.0	0.4	0.4	0.2	0.1		5	12	5	95	10	98

[a] Analyses on uranium basis.

[b] Reduction at 500°C., hydrofluorination at 410°C.

[c] Did not reach 97% conversion.

Thermogravimetric Evaluation of Ore Concentrates. The purified ore concentrates prepared in the leaching tests just described have been evaluated in the laboratory thermobalance. The results of the tests, table F-14, showed highly variable conversion efficiencies during both the hydrogen reduction at 930°F. and the hydrofluorination of the contained uranium to uranium tetrafluoride at 770°F. For twenty-one of the concentrates, the reduction in hydrogen was complete in 6 to 20 minutes, the latter time being the same as that required to reduce a composite sample of Hanford continuous-calciner oxides. The remaining five concentrates required longer times for reduction, and one stopped reacting at about 60% completion after 40 minutes.

Conversion of 98% of the contained uranium to uranium tetrafluoride at 770°F. was observed in the case of eleven of the reduced ore concentrates, nine of which were hydrofluorinated in less than

the 47 minutes required for the Hanford oxide. Less than 20 minutes total time was required for both the reduction and hydrofluorination of the four most reactive concentrates. The contained uranium in the reduced product from seven additional concentrates was converted to above 90% uranium tetrafluoride.

The concentration of volatile components in the concentrates, such as water, ammonia, and nitrogen oxides, was shown to vary from 0.3 to 19.5% during heating in flowing helium for 10 minutes at 930°F. Compounds producing volatile fluorides in these ore concentrates varied from 0 to 8.7%. A correction factor taking these variations into account was applied to all conversions using the method previously reported .

Purification of Ore Concentrate Uranium Hexafluoride. As reported previously , pilot-plant studies have been directed toward development of selective sorption as an alternate to distillation for removal of vanadium and molybdenum from uranium hexafluoride. Two tests were made during the report period to evaluate fluorinated alumina and sodium fluoride for this use.

Approximately 300 pounds of uranium hexafluoride having average vanadium and molybdenum concentrations of 40 and 12 ppm., respectively, was fed through a 4-foot deep bed of fluorinated alumina in a 3-inch diameter column at an average feed rate of 8 pounds per hour. The surface area of the sorbent was 40 sq.m./g., and the aluminum fluoride content was 30%. Outlet gas analyses indicated that the vanadium concentration was reduced to approximately the 1 ppm. specification, except during brief periods of high impurity concentration and feed rate. Molybdenum removal was poor, however, with an initial efficiency of 25% which then decreased slowly to zero. The quantity of molybdenum stripped from the uranium hexafluoride was estimated by difference to be 21 mg. per pound of fluorinated alumina.

Since the quantity of ore concentrate uranium hexafluoride available for sorption tests was limited, it was decided to forego complete vanadium capacity data (estimated to be more than 200 mg. of vanadium per pound of fluorinated alumina) and to determine instead if the bed could be regenerated. The initial regeneration attempt was made with fluorine at 300°F. Gas samples taken during the fluorination showed outlet concentrations of 4 to 8% uranium hexafluoride, less than 10 to 330 ppm. vanadium, and 1 to 9 ppm. molybdenum. An attempt to regenerate further at 600°F. resulted in additional fluorination of the solid, a temperature rise to 1050°F., and partial fusion of the charge.

In a second sorption test, a 1-inch column was charged to a height of 81 inches with 2.5 pounds of sodium bifluoride pellets. The bed was heated in an air stream to drive off hydrogen fluoride, and the sodium fluoride remaining was saturated with 10 pounds of pure uranium hexafluoride. A total of 89 pounds of the impure uranium hexafluoride was passed through the bed at an average feed rate of 1.9 pounds per hour with the system maintained at 250°F. Incomplete analytical data indicate a bed capacity of more than 1.3 grams of vanadium per pound of sodium fluoride, but outlet gas analyses of 2.2 ppm. vanadium show too few transfer units to reach the 1 ppm. specification. Feed and effluent analyses showed that molybdenum was not removed from the gas stream. Tests with the sodium fluoride will be continued.

Since the sorbents evaluated to date have shown appreciable capacity for vanadium but little ability to sorb molybdenum from ore concentrate uranium hexafluoride, other materials, potassium fluoride, lithium fluoride, calcium fluoride, and 5A molecular sieves, have been tested in bench-scale equipment. The measurements obtained indicate that only potassium fluoride warrants further study.

RECOVERY OF URANIUM FROM MAGNESIUM FLUORIDE SLAG

Large quantities of magnesium fluoride slag containing about 5% uranium and small amounts of magnesium metal and magnesium oxide are generated in the production of normal uranium metal. Previously reported studies at the Oak Ridge Gaseous Diffusion Plant indicated that direct fluorination employing either vibrating-tray or fluid-bed reactors was a feasible means of recovering the uranium from this material. The slag, after treatment, was a dry, high purity magnesium fluoride which might be used by industry; e.g., as a raw material in the preparation of hydrogen fluoride.

When the Atomic Energy Commission recently requested cost estimates for processing slag at rates ranging from 630 to 1,730 pounds of bulk per hour (21 to 105 pounds contained uranium) by the fluorination technique, an evaluation of the economic and technical feasibility of employing available equipment was made. The result of this study was a proposal based on the use of a multiple hearth vertical reactor which had been employed at the Oak Ridge Gaseous Diffusion Plant for the production of uranium tetrafluoride from uranium dioxide. Use of the vertical reactor appeared advantageous for the following reasons:

1. The unit is constructed of Monel; thus, expensive rebuilding required for trays or screws which are made mainly of Inconel, an alloy not suitable for use in fluorine at elevated temperatures, is avoided.

2. The reactor is no longer required for hydrofluorination and is available for the proposed use without disrupting present programs. This is particularly valuable in comparison to screw lines which, according to feed schedules, will be needed for uranium tetrafluoride production, both at Oak Ridge and Paducah.

3. The contacting efficiency is probably sufficient to allow processing of slag at the maximum rate, and it has been shown by dry runs that the conveying capacity is adequate. Based on pilot-plant tests, one tray line probably does not have sufficient capacity to give satisfactory stripping at the maximum feed rate. While one screw line might be adequate, flight redesign to move the material at a volume rate considerably in excess of that reached with uranium powders would be necessary.

4. The reactor construction and space requirements are such that it is feasible to relocate it to provide economical material handling, particularly when grinding of the slag on site is required.

5. The operating cost, as derived from previous experience, is less than for one tray or screw line.

Two short fluorination tests have been made with Paducah slag containing about 6% uranium to evaluate the performance of the vertical reactor. Fluorine plant product gas containing about 92% fluorine was used in both cases. In the first run, powder was fed for 1.5 hours at a rate of 830 pounds per hour, and the reactor operated satisfactorily; however, difficulties with the temporary feeding arrangement caused termination of the run. Since the powder residence time as previously

measured in radioactive tracer tests is 0.5 hour, about three reactor throughputs were obtained. The stripped slag analyses of 0.3 to 0.85% uranium were felt to be encouraging, but not representative of continued operation because unfluorinated powder was used to obtain a seal in the product hopper.

After revision to the loading system, the unit was operated for 1.6 hours at a rate of 1,030 pounds of magnesium fluoride per hour. The uranium content of the stripped slag ranged from 0.2 to 0.7% uranium and averaged 0.4%. It is felt that somewhat better stripping would be obtained if temperatures were increased from the maximum of 750°F. used in this run and the slag were ground finer than the Paducah material which contained 40% greater than 200-mesh particles. It is also possible that decreasing the agitator speed would increase the residence time and thus improve stripping. The ease with which the powder temperature was controlled in both tests indicates that no difficulty would be encountered with processing rates higher than those studied.

In connection with slag processing, the Mallinckrodt Chemical Works has requested the Oak Ridge Gaseous Diffusion Plant to fluorinate 15 tons of uranium-bearing, magnesium fluoride slag for use as a liner in the metal reduction bombs. To fluorinate this material, the feed system to the reactor must be modified to eliminate the dust problem on the operating floor and to provide a better seal against fluorine leakage. In addition, a 2-inch line from the column to a recycle pump in the uranium hexafluoride system will be necessary to transport the outlet gases to the feed plant cold traps. The estimated operating and capital expenditures were presented to the Mallinckrodt Chemical Works for their consideration. It appears that production can be initiated within two weeks and that the 15 tons can be processed in approximately two days.

PREPARATION OF HYDROGEN FLUORIDE FROM MAGNESIUM FLUORIDE BOMB SLAG

A study has been initiated to investigate the possibility of utilizing magnesium fluoride as a raw material in the manufacture of anhydrous hydrogen fluoride. Bench-scale, batch tests have been made to compare the reactivities of minus 325-mesh fluorinated bomb slag and calcium fluoride when treated with 96% sulfuric acid at elevated temperatures. The results indicated that, under identical operating conditions, the slag was considerably less reactive than calcium fluoride; however, by increasing the sulfuric acid excess and reaction time and temperature, it was possible to volatilize as much as 90% of the fluoride content of the slag. It was also found that the reacted portion of the slag (magnesium sulfate) could be dissolved easily leaving a fine magnesium fluoride which was as reactive as the original material. Since the operating conditions required to obtain a 90% yield of hydrogen fluoride from the slag could apparently be met readily in plant-size equipment, a pilot-plant which will permit a realistic evaluation of a continuous process is being designed.

GAS PHASE HYDROLYSIS OF URANIUM HEXAFLUORIDE

It has been recognized that a considerable saving would be realized in the cost of containers if the depleted uranium from the gaseous diffusion complex could be stored as a solid in conventional open-top drums rather than as uranium hexafluoride in large steel cylinders. Some of this material is now being converted to uranium tetrafluoride by reduction with hydrogen and one-third of the fluoride value is being recovered as hydrogen fluoride. It is apparent, however, that two-thirds of the fluorine could be recovered if the uranium hexafluoride were converted to uranyl fluoride by reaction with water. Consequently, a cursory investigation of this reaction was made in the 4-inch diameter pilot-plant tower reactor.

The pilot plant consisted of a uranium hexafluoride vaporizing and metering station, a steam metering station, a steam superheater, a tower reactor, and an off-gas filter. The reactor was a 10-foot length

of 4-inch diameter Monel pipe mounted vertically and heated electrically by beaded Nichrome wire. In operation, gaseous uranium hexafluoride and superheated steam were introduced at the top of the reactor through a concentric jet type mixer, and the solid product was collected in a receiver at the bottom of the unit. The off-gases passed through a dust filter and discharged into a neutralization pit.

For the first test, the unit was operated with a wall temperature of 350°F., a uranium hexafluoride rate of 13 pounds per hour, and a steam excess of 100%. A porous carbon tube filter was used to separate the entrained solids from the off-gases. During the 3-hour operating period, there was no evidence of a localized heat release in the tower; the uranyl fluoride product was light yellow in color and had a packed density of 0.24 g./cc. Inspection of the system showed that a considerable quantity of soft powder had accumulated on the tower walls and had almost plugged the unit completely at a point approximately 4 feet below the mixer nozzle. The off-gas filter was plugged, and the lower 1/2 inch of the carbon tube had disintegrated, probably as a result of reaction with uranium hexafluoride.

In an attempt to increase the product density by reaching a higher reaction temperature, a second test was performed with a higher uranium hexafluoride feed rate of 48 pounds per hour, a water excess of 83%, and a reactor wall temperature of 840°F. For this run, the carbon filter was replaced with a Monel wire cloth filter packed with Monel wool. The test was stopped after 25 minutes of operation due to the formation of a plug in the system. As in the first run, no evidence of a localized heat release was obtained. Inspection of the reactor showed that the top portion was filled with a soft cake of powder. Uranyl fluoride had also deposited in the outlet gas lines, thus indicating that uranium hexafluoride had passed through the filter and had reacted in the exit lines.

No further investigation of the hydrolysis reaction is planned at the present time. Sufficient information has been obtained in the studies described above to aid in evaluation of the over-all storage problem.

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During the quarter, the greater portion of the feed development program was concerned with the direct processing of ore concentrate to pure uranium hexafluoride. Studies included pilot plant evaluation of various reactors for the fluorination of impure uranium tetrafluoride and further evaluation of sorption of molybdenum and vanadium from uranium hexafluoride by solid compounds. In addition, work on the preparation of hydrogen fluoride from magnesium fluoride bomb slag was continued.

ORE CONCENTRATE PROCESSING

Fluorination Studies

It was apparent in the Paducah feed plant tests that rapid plugging of the fluorination tower outlet gas line would prevent efficient operation with the uranium tetrafluoride prepared directly from Rand ore concentrate. A pilot-plant program was initiated, therefore, to determine the suitability of alternate reactor systems for the fluorination of this material. Tests with a scraped cooler in the tower outlet gas line and with a fluid-bed reactor have been completed; additional studies with a large diameter tower are planned.

The impure uranium tetrafluoride was fluorinated at rates up to 62 pounds of uranium per hour in the 4-inch diameter pilot-plant tower which is equipped with a 6-inch diameter scraped cooler. During 43 hours of operation, no plugging was observed in the cooler, but fused material collected in the reactor at a rate of 0.04 pound per pound of uranium reacted. The slag apparently deposited as a viscous liquid and formed a smooth layer around the tower wall with the largest accumulation at the bottom. Analysis of material removed from the walls showed primarily the impurities present in the starting uranium tetrafluoride with only a small percentage of the uranium remaining.

Additional studies with a much larger diameter tower are planned. It is hoped that increasing the distance from the reaction zone to the walls will allow the molten particles to solidify and thus prevent caking. A 16-inch diameter tower has been constructed and will be tested in the near future.

Tests were also made in a 6-inch diameter fluid-bed reactor with powder feed and discharge points at the top of the bed. Employing a feed mixture of 5% minus 40 plus 200-mesh magnesium fluoride and 95% impure uranium tetrafluoride, rapid caking of the 30-inch deep bed, and a loss of fluidization occurred at an operating temperature of 1000° F. With the magnesium fluoride diluent increased to 20%, however, and the temperature lowered to 900°F., the unit performed well for about 6 hours at a processing rate of 84 pounds of uranium per hour per cubic foot of bed. Approximately 99% of the uranium fed was converted to uranium hexafluoride.

Inspection of the bed at the completion of the run showed a small quantity of large sintered particles. It is probable, however, that a bottom discharge would effectively prevent accumulation of these lumps. Raising the operating temperature to 1000°F. increased the amount of sintering; tests were not made at lower temperatures.

Purification of Uranium Hexafluoride

As reported previously, the pilot plant program has been directed toward development of selective sorption as an alternate to distillation for removal of vanadium and molybdenum from uranium hexafluoride. During the report period, sodium fluoride has been evaluated for this use.

Studies were made in a 1-inch diameter column with an 8-1/2-foot deep bed of porous sodium fluoride pellets which had been prepared by heating sodium bifluoride pellets to 850°F. in an air stream. A bed temperature of 250°F. was employed, and before starting a sorption run, the pellets were saturated with uranium hexafluoride by treatment with either pure reactor tails or impure normal

assay material. The uranium hexafluoride used for the tests included both material purchased from General Chemical Company and that prepared from ore concentrate in the K-1413 pilot plant. Vanadium and molybdenum concentrations in this feed ranged from 125 to 7,000 and from 100 to 3,000 ppm., respectively.

The impure uranium hexafluoride was passed through the sodium fluoride at rates of 110 to 350 pounds per hour per square foot of bed until colorimetric vanadium and molybdenum analyses on effluent gas samples indicated the solid was saturated. The bed was then regenerated by raising the temperature to 750°F. for about 8 hours while adding fluorine, and after cooling to 250°F., the sorption cycle was repeated. Estimates of the quantities of impurities sorbed and desorbed were based on the analyses of feed and effluent gas samples. The results of the tests are summarized below:

1. The sorptive capacity at 250°F. of a new bed of sodium fluoride was approximately 5 grams of vanadium and 1 gram of molybdenum per pound of sodium fluoride. After three sorption-desorption cycles, vanadium and molybdenum capacities were reduced by about 75 and 90%, respectively. No further reduction in capacity was noted after three additional cycles. Assuming the vanadium capacity were not reduced further, a bed life of twenty sorption-desorption cycles would be required to decrease the sodium fluoride cost to $0.01 per pound of uranium for a uranium hexafluoride feed containing 1,000 ppm. vanadium. Employing a similar assumption for molybdenum, a bed life of sixty cycles would be required for a uranium hexafluoride feed containing 200 ppm. molybdenum.

2. Under conditions of relatively low flow and impurity concentration in the feed, the 8.5-foot deep sodium fluoride bed removed sufficient vanadium to produce an effluent stream which, according to spectrographic analyses, met the 1 ppm. specification. This bed was not tall enough, however, to reduce the effluent molybdenum concentration below 40 ppm. for any prolonged period.

   The height of a mass transfer unit was estimated for vanadium by the method of Hougen and Marshall* at various feed rates. The maximum height obtained was 3.8 inches with most values falling in the range between less than 0.1 inch at 133 pounds per hour per square foot and 0.7 inch at 350 pounds per hour per square foot.

3. The loss of sorptive capacity corresponded roughly to the decrease in surface area, from 2.3 to 0.4 sq.m./g., after one sorption-desorption cycle. Much of this measured surface is within the sodium fluoride pellet, however, and is probably not utilized for sorption under normal operating conditions. This conclusion is based on a test with a bed which had been saturated with vanadium and then allowed to stand for 24 hours. A renewed capacity of the bed indicated that the vanadium compound had diffused into the sodium fluoride pellet and partially regenerated the outer surface.

4. The uranium hexafluoride sorbed by the sodium fluoride bed exchanged with that in the feed stream very slowly.

5. In the presence of a fluorine bleed, both vanadium and molybdenum, as well as uranium, were desorbed effectively from a sodium fluoride bed at 750°F. These materials were desorbed partially at temperatures as low as 450°F.

6. Failure to top the cylinder to remove hydrogen fluoride resulted in plugging of the bed due to the formation of low melting complex fluorides of the form NaF·X (HF).

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* Hougen, O. A., and Watson, K. M., *Chemical Process Principles*, John Wiley and Sons, New York, p. 1081 (1947).

In view of the relatively poor performance of the sodium fluoride with respect to molybdenum removal, studies with this material have been discontinued. Bench-scale tests with other solid compounds are planned in an effort to discover an efficient trapping medium for molybdenum.

RECOVERY OF HYDROGEN FLUORIDE FROM MAGNESIUM FLUORIDE BOMB SLAG

Upon completion of the bench-scale batch tests reported previously, a pilot-plant facility was constructed to investigate the continuous recovery of hydrogen fluoride from ground magnesium fluoride bomb slag by reaction with concentrated sulfuric acid at elevated temperatures. An equipment flow sheet of the installation, designed to process approximately 10 pounds per hour of ground slag, is shown in figure F-13. The unit consists essentially of an electrically heated, paddle agitated, horizontal steel pipe reactor provided with means for (1) continuous feeding of sulfuric acid and bomb slag; (2) continuous take-off, scrubbing and condensation of the gaseous reaction products; and (3) semi-continuous discharge of the solid reaction product.

In operation, concentrated sulfuric acid and finely divided magnesium fluoride bomb slag are metered continuously into a steel mix tank which is equipped with an air driven, turbine-type agitator. The resulting thin slurry is gravity fed through an overflow pipe and seal leg into the vapor take-off end of the 6-foot long, 8-inch diameter heated pipe reactor where the following endothermic reaction occurs:

$$MgF_2 + H_2SO_4 \rightarrow MgSO_4 + 2\ HF$$

The reactor off-gases, containing hydrogen fluoride, as well as varying amounts of dust, water, sulfuric acid, and sulfuric acid reduction products, are passed first through a Raschig ring packed tower to remove the entrained dust and to scrub the gases with condensed water and sulfuric acid, then through a water-cooled partial condenser to remove additional water and sulfuric acid, and finally, into a dry ice-cooled trap which serves as a total condenser to remove the hydrogen fluoride product. Provision is made in the acid piping system to feed all or part of the feed acid into the top of the packed tower to scrub the reactor off-gases. The dry, free-flowing solid reaction product, which consists primarily of magnesium sulfate containing unreacted magnesium fluoride and sulfuric acid, is discharged into an electrically heated receiver.

The results of tests completed to date are promising in that it has been possible to volatilize more than 90% of the contained fluoride from minus 325-mesh (6-micron average particle size) fluorinated magnesium fluoride slag by reaction with concentrated (99%) sulfuric acid at temperatures ranging from 300°F. at the feed end of the reactor to 700°F. at the solids discharge end. The degree of conversion appears to be greatly influenced by the particle size of the solid feed, since only 70% of the contained fluoride was volatilized from minus 200-mesh (20-micron average) material under similar operating conditions. The test results also indicated that it would be desirable to use at least 100% sulfuric acid as the acid feed, since any water added to the system serves to dilute the liquid product and apparently causes caking in the reactor and severe corrosion of the agitator blades near the feed point. An undesirable result found in the present investigation has been the appearance of varying amounts of sulfur dioxide in the cold trap product indicating sulfate reduction, possibly by the steel system or by the residual uranium and magnesium metal in the solid feed material; however, since it is planned to roast the bomb slag in an oxidizing atmosphere prior to treatment with fluorine to recover uranium, and since elimination of water from the system should minimize corrosion of the steel, it is felt that the generation of sulfur dioxide will not be a serious problem in a plant-scale unit.

In all of the tests completed to date, a substantial proportion of the excess sulfuric acid fed left the reactor with the solid product. In each case, however, most of the contained acid was driven off by heating the product to 800°F. for 2 hours, indicating that it may be possible to operate with a considerably lower over-all acid excess if the vaporized acid can be recovered and reused.

Additional tests are planned to determine the optimum operating conditions for generation and recovery of the hydrogen fluoride and to investigate the possibility of using unfluorinated bomb slag as the feed material.

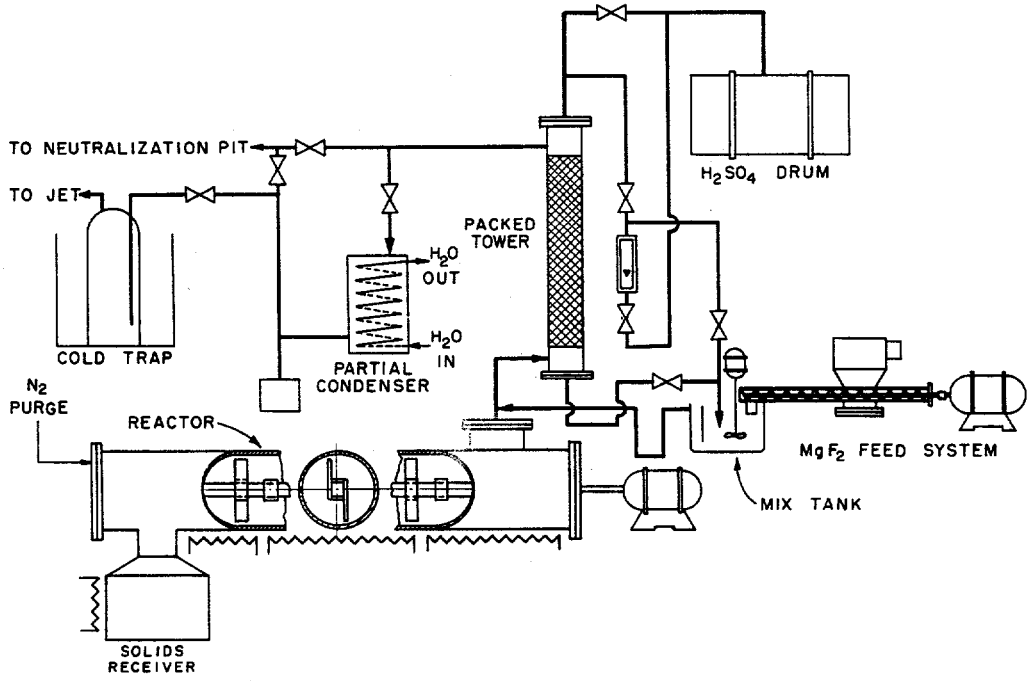

FIGURE F-13
HF Recovery Pilot Plant

JANUARY 1, 1959, THROUGH MARCH 31, 1959

The development effort on feed manufacture and related projects decreased considerably during the quarter. Studies of the preparation of hydrogen fluoride from magnesium fluoride bomb slag were continued. No further work was done on the direct processing of ore concentrate.

RECOVERY OF HYDROGEN FLUORIDE FROM MAGNESIUM FLUORIDE BOMB SLAG

Studies of the preparation of anhydrous hydrogen fluoride by the reaction of sulfuric acid with magnesium fluoride bomb slag were continued in the pilot-plant facility described previously. The major purpose of the work completed to date has been to determine the effect of operating conditions on the amount of fluoride converted to hydrogen fluoride and on the composition of the gaseous product. Investigations of methods of purifying the hydrogen fluoride and of preparing a commercially desirable product from the solid residue are planned but have not been started.

In general, it has been shown that, with sulfuric acid excesses of about 100% and a maximum reactor temperature of 500°F., 90% or more of the fluoride in finely ground bomb slag can be converted to hydrogen fluoride. To reduce corrosion and to minimize the amount of water in the gaseous product, it is necessary to use a completely anhydrous acid feed. The gases evolved from the reaction contain small amounts of sulfur dioxide, sulfuric acid, and water, in addition to hydrogen fluoride; the solid residue remaining after treatment is apparently the acid salt of magnesium sulfate and has a sulfuric acid content of about 40%.

The results of tests made with various magnesium fluoride particle sizes, sulfuric acid excesses and concentrations, and temperatures are summarized in table F-18. Both magnesium fluoride from which the uranium had been removed by fluorination and untreated slag were studied, and in all of the runs, the solids feed rate was 5 pounds per hour. It can be seen from the data that it is difficult to define clearly the effects of most of the operating variables. The erratic results are probably due to caking in the reactor which caused variable residence times and to difficulty in sampling the volatile product. Some general conclusions can be drawn from the pilot-plant experience, however, and are discussed below.

Reactor Performance. Trouble was experienced with caking of the solid product in the paddle-type reactor, and usually, it was necessary to clean the unit after about 16 hours. It is felt, however, that the durations of the runs were sufficient to permit a preliminary evaluation of the process. For production purposes, use of a rotary kiln containing loose metal rods would probably prevent caking.

Magnesium Fluoride Particle Size. Tests were made with pulverized fluorinated slags having maximum particle sizes of 20, 30, and 100 microns. In this size range, there appeared to be little difference in the extent to which the fluoride was converted to hydrogen fluoride. Studies were not made with larger particle sizes.

Sulfuric Acid Excess. A definite trend showing improved conversions to hydrogen fluoride with increased sulfuric acid excesses was observed; an excess of about 100% was required for greater than 90% conversion. No consistent effect of acid excess on the outlet gas composition was shown, but higher acid contents of the solid residues were noted with increased acid feeds.

TABLE F-18

Summary of Pilot Plant Studies of the Preparation of Hydrogen Fluoride from Magnesium Fluoride Bomb Slag

Run Number	Length Of Run, hours	H_2SO_4 Concentration, %	H_2SO_4 Excess, %	Reactor Temperature, °F.(a)	MgF_2 Reacted, %	Outlet Gas Analyses, weight percent				H_2SO_4 Content Of Solid Product, %
						HF	H_2O	SO_2	H_2SO_4	
	Fluorinated Slag; Average Particle Size = 12 Microns; Maximum Particle Size = 100 Microns									
4	10.2	93.0	21	300 - 700	63.2	73.3		6.4	3.4	22.6
7	7.2	93.0	56	300 - 500	64.1	62.2	36.0	1.8	1.0	38.2
8	8.5	93.0	59	300 - 500	60.0	61.9	38.0	0.8	0.5	35.7
46	8.2	100.3	155	300 - 500	94.0	72.7	2.2	5.7	20.8	51.3
47	6.0	100.3	132	340 - 480	88.0	73.1	1.2	8.9	12.1	49.6
	Fluorinated Slag; Average Particle Size = 8 Microns; Maximum Particle Size = 30 Microns									
26	8.9	100.7	77	300 - 700	82.7	59.4	5.6	19.4	3.1	36.5
28	7.5	100.7	22	300 - 700	53.0	87.8	3.5	5.0	4.8	21.1
29	7.3	100.5	96	300 - 700	74.0	83.1	4.2	6.7	3.5	31.7
31	8.0	101.7	45	300 - 700	84.0	76.0	3.4	12.7	7.0	51.7
33	8.0	101.7	51	300 - 700	83.0		1.8		4.4	31.7
	Fluorinated Slag; Average Particle Size = 7 Microns; Maximum Particle Size = 20 Microns									
15	8.8	99.5	56	300 - 700	74.6	76.7	23.0	4.3	2.3	27.2
16	7.0	99.5	60	300 - 700	73.2	69.9	28.4	4.6	7.0	26.4
17	7.0	99.5	60	300 - 700	80.0	74.1	18.0	1.5	6.9	29.3
23	7.9	98.5	86	300 - 600	63.8	63.8	9.3	0.5	7.5	41.0
38	5.0	100.6	110	400 - 500	93.0					42.4
39	5.8	100.6	85	400 - 500	89.0	76.4	1.9	4.4	14.6	42.5
40	7.0	100.6	22	450 - 500	73.0					32.9
42	4.8	100.6	48	420 - 500	74.0					38.2
43	8.0	100.1	100	300 - 500	93.0	86.0	2.1	3.5	1.3	45.1
	Untreated Slag; Average Particle Size = 35 Microns; Maximum Particle Size = 250 Microns; Uranium Content = 5%									
9	8.5	98.9	61	300 - 750	57.8	74.5	4.0	15.1	6.4	32.9
10	9.3	98.9	75	300 - 700	67.1	55.3	19.0	21.6	5.3	41.8

(a) Temperatures graded from feed end to powder discharge.

Sulfuric Acid Concentration. The amount of water evolved from the reactor decreased as the sulfuric acid concentration increased; however, even with 100% acid, the water content of the outlet gas was appreciable. Visual inspection of the reactor agitator after operation with 93% acid showed considerably more corrosion that was experienced with 100% acid.

Temperature. In the range studied, 400 to 700°F., no significant effect of maximum reactor temperature on the conversion to hydrogen fluoride was found. Some lowering of the sulfur dioxide content of the gaseous product appeared to be accomplished, however, by decreasing the operating temperature from 700 to 500°F. Tests were not made at lower temperatures, since earlier batch experiments had indicated that reaction rates were very slow below 400°F.

Solid Residue. The solids discharged from the reactor were free flowing but were quite hygroscopic and caked badly on exposure to wet air. The sulfuric acid content of the residue ranged from 21 to 52% and could be reduced to less than 5% by heating to 800°F. for 2 hours. Tests have not been made to determine if the gases evolved can be recovered as usable acid by scrubbing with concentrated sulfuric acid.

Slag Fluorination. In the tests with untreated slag, the concentrations of sulfur dioxide in the outlet gas were high. It is possible that reactions involving uranium or magnesium metal are responsiboe for the formation of the additional sulfur dioxide.

APRIL 1, 1959 THROUGH JUNE 30, 1959

RECOVERY OF HYDROGEN FLUORIDE FROM URANIUM HEXAFLUORIDE

Large quantities of depleted uranium hexafluoride, cascade tails, are generated by the gaseous diffusion plants. Some of this material is presently being processed at the Paducah metals plant to recover a portion of the fluoride content as anhydrous hydrogen fluoride by reduction with hydrogen, while the remainder is being stored in cylinders as uranium hexafluoride. Since only one-third of the available fluoride is removed by the reduction method, alternate processes, in which complete fluoride recovery is possible, are being studied.

Potentially feasible reactions by which this might be accomplished are reduction-hydrolysis and hydrolysis as represented by the following equations:

$$UF_6 + 2\,H_2O + H_2 \longrightarrow UO_2 + 6\,HF \qquad \Delta H_{298} = 23.8 \text{ kcal.}$$

$$UF_6 + 3\,H_2O \longrightarrow 1/3\,U_3O_8 + 6\,HF + 1/2\,O_2 \qquad \Delta H_{298} = +\,8.7 \text{ kcal.}$$

Laboratory studies in a tower reactor at Paducah* and fluid-bed tests at Argonne National Laboratory** have shown that the reaction with hydrogen and steam will proceed at a reasonable rate if temperatures of about 1200°F. are employed. The uranium oxide formed was relatively dense and free-flowing. Similar tests at Paducah indicated that the hydrolysis reaction was also feasible, but that temperatures of about 1600°F. were required.

In view of the encouraging results of the laboratory investigations, it was decided to study both processes in an existing pilot-plant fluid-bed reactor. This type of unit was selected because of its high volumetric efficiency and good heat transfer characteristics. The initial tests are being made with both hydrogen and steam, since the lower operating temperature and smaller heat requirement make this method more attractive from a production standpoint.

A schematic diagram of the pilot-plant system is shown in figure F-5. The unit consists of an electrically heated, 6-inch diameter, fluid-bed reactor, equipped with a conical bottom for gas distribution; metering systems for uranium hexafluoride, steam, and hydrogen; parallel sintered metal filters to separate the gaseous and solid products of the reaction; and a water scrubber to remove the product hydrogen fluoride from the excess hydrogen before venting to the atmosphere. For production, the scrubber would be replaced with a suitable condenser to recover the product hydrogen fluoride.

Uranium oxide powder is charged into the reactor and is fluidized by a mixture of hydrogen and water vapor. Uranium hexafluoride is then introduced near the bottom of the bed through the inner channel of a concentric nozzle; a flow of about 0.5 cfm. of nitrogen is maintained in the annulus to minimize the possibility of plugging the nozzle. The reaction takes place in the powder bed, which has a volume of 1/2 cubic foot, and the uranium oxides and hydrogen fluoride formed pass out of the reactor through an overhead discharge pipe to the filter system. Two filter tubes are used alternately so that the operation is not interrupted during backblowing of the filter. The solid product is collected in a receiver located directly below the filter and is removed periodically. After filtering, the reaction gases are sampled and then scrubbed before being vented to the atmosphere.

The results of the tests made to date are summarized in table F-10. Bed temperatures of 1100 to 1270°F. and feed rates of 17.0 to 22.8 pounds of uranium per hour per cubic foot of bed were employed, and in all cases, only trace quantities of uranium, 1 ppm. or less, were found in the scrubber liquid. The extent of hydrogen fluoride recovery was influenced greatly by the operating

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* Bernstein, S., Thomas, R. J., and Lisso, M. S., *Operations Division Engineering Progress Report, February, 1959*, Union Carbide Nuclear Company, Paducah Gaseous Diffusion Plant, April 20, 1959 (KY-286).

** Personal communication from A. A. Jonke.

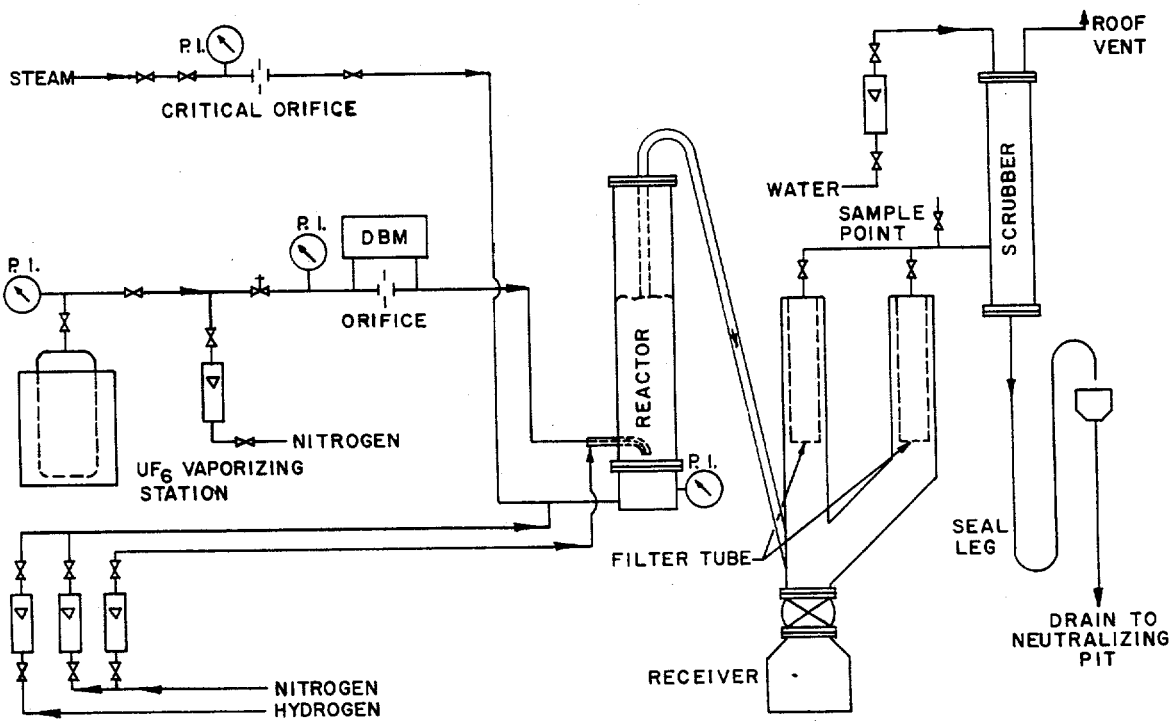

FIGURE F-5
Schematic Flow Diagram HF Recovery Pilot Plant

temperature with fluoride concentrations in the solid product ranging from 12.8 to 2.5%, respectively, for tests at 1100 and 1270°F. The density of the solid product also increased with increasing temperature; packed densities ranging from 21 to 225 pounds per cubic foot were obtained. The low density material appeared to be uranyl fluoride from fluoride analyses.

The system performed well during the tests; however, sieve analyses of the solid product from the 28.5-hour run showed that the average particle size increased significantly as the run progressed. This particle growth was also indicated by internal temperature measurements which showed a gradual decrease in bed fluidity. Modification of the reactor to provide a bottom instead of a top solids discharge should eliminate this problem.

It is planned to continue the tests to optimize the operating conditions and to determine the capacity of the unit. Emphasis will be placed on the use of low steam and hydrogen excesses. Upon completion of this phase of the program, studies of the reaction with steam only will be made. Since these methods should be convenient for the preparation of uranium dioxide from uranium hexafluoride of various assays, the solid products from the tests will be examined for potential application to preparation of oxide fuels.

TABLE F-10
Recovery of Hydrogen Fluoride from Uranium Hexafluoride

Run Number	Feed Rate, lb. U/hr./cu.ft.	H_2 Excess, %	Water Excess, %	Average Bed Temp., °F.	Product HF Conc., Wt. %	Fluoride In Product Oxide, Wt. %	Fluoride Recovery, %	Product Oxide Bulk Density, lb./cu.ft.	Product Oxide Packed Density, lb./cu.ft.	Running Time, hours
1	17.0	139	69	1130	72.5	12.4	66.6	10	21	8.0
2	22.8	80	67	1100	74.7	12.8	65.3	25	37	6.1
3	18.1	128	39	1200	83.3	9.9	73.6	106	175	3.9
4	17.7	172	75	1270	82.0	2.5	93.7	175	225	28.5

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